

TREATMENT OF SYNTHETIC WASTEWATER
BY ZIF-8, ZIF-67, AND ALUMINUM
NANOCOMPOSITES

BY

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This thesis work is dedicated to my dear mother, “Aisha Salem Abdullah Al-Qathmi.”

|

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LIST OF ABBREVIATIONS

ANTs	Aluminum Nanotubes
MOFs	Metal Organic Frameworks
ZIFs	Zeolitic Imidazole Frameworks
WHO	WHO World Health Organization
ppm	Part Per Million
BET	Brunauer-Emmett Teller
FTIR	Fourier Transform Infrared
XRD	X-Ray Diffraction
S_{BET}	BET Specific Surface Area
V_{P}	Specific Pore Volume
d_{P}	pore Size
Zn	Zinc
Co	Cobalt
2-MIM	2-Dimethylimidazole
ZIF-8	Zeolitic Imidazole Framework-8
ZIF-67	Zeolitic Imidazole Framework-67
ANTs@ZIF-8	Functionalized Aluminum Nanotubes with Zeolitic Imidazole Framework-8
ANTs@ZIF-67	Functionalized Aluminum Nanotubes with Zeolitic Imidazole Framework-8
CR	Congo Red

CV	Crystal Violet
TC	Tetracycline
MB	Methyl Blue
MB	Methyl Blue
MR	Methyl Red
MO	Methyl Orange

|

ABSTRACT

Full Name : Ibrahim Ali Basfer

Thesis Title : Treatment of Synthetic Wastewater by ZIF-8, ZIF-67, and Aluminum Nanocomposite

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One of the most challenging environmental issues in the world is the disposal of industrial waste into the marine environment, which requires an immediate response. This has resulted in an increase in pollution, which is harmful to both the ecosystem and human health. Adsorption is a very promising and inexpensive approach for contamination treatment; nevertheless, the potency of this approach demands the development of efficient adsorbents. In this research, two novel adsorbents (ANTs@ZIF-67 and ANTs@ZIF-8) were synthesized and applied for the removal of congo red, crystal violet, and aspirin from water bodies. The surface properties, structure, and morphology of all prepared adsorbents were investigated by Fourier transform infrared (FTIR) spectroscopy, N_2 adsorption, and X-ray diffraction. After that, the impacts of contact time, initial pollutant concentration, temperature, and pH on the removal performance of these two adsorbents were investigated. The kinetic studies demonstrated that the Avrami model accurately fitted the experimental results for CR, CV, and aspirin removal of 1039, 1786, and 811 mg/g, respectively. Furthermore, the adsorption isotherms revealed that the Redlich-Peterson model precisely predicted the isotherm data for the removal of CR, CV, and aspirin, with R^2 values almost equal to unity. The thermodynamic investigations stated the endothermicity and spontaneous nature of CR and CV adsorption with positive values of ΔH and ΔS properties, while aspirin exhibited exothermic adsorption behavior. Another interesting result found herein is the high stability and reusability of these nanocomposites, as illustrated by the minor reduction in CR, CV, and aspirin removal after five adsorption-desorption cycles. Ultimately, the findings from this work illustrate that aluminum-based zeolitic imidazolate frameworks possess promising adsorbents for dyes and pharmaceuticals removal from synthetic wastewater samples.

ملخص الرسالة

الاسم الكامل: إبراهيم علي عبدالله بصفر

عنوان الرسالة: معالجة مياه الصرف الصناعية المعقدة بواسطة مركبات نانوية جديدة ذات أساس معدنية

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تتعلق إحدى القضايا البيئية الأكثر تحدّيًا في العالم بالنفايات السائلة وتتطلب استجابة فورية حيث إن الطريقة الأسهل للتخلص من هذه الملوثات البشرية والصناعية هي بتصريفها في البيئة البحرية. وقد أدى ذلك إلى ارتفاع معدلات التلوث، وهو ما يضر بالنظام البيئي وصحة الإنسان. يعد الامتزاز تقنية واعدة للغاية وغير مكلفة لمعالجة هذا التلوث ومع ذلك فإن فعالية هذا الطريقة تتطلب تطوير مواد مازة فعالة. في هذا البحث تم تصنيع مادتين ممتزتين جديدتين هما ANTs@ZIF-67 و-ANTs@ZIF-8 وتطبيقهما لإزالة كلا من الصبغ CR والصبغ CV بالإضافة إلى مادة الأسبرين من المحاليل المائية.

في البداية تم دراسة الخصائص التركيبية والمجموعات الوظيفية وبعض الخصائص الأخرى المهمة لجميع المواد المازة المحضرة بواسطة التحليل الطيفي (FTIR) وامتزاز النيتروجين وحيود الأشعة السينية (XRD). بعد ذلك، تم دراسة تأثير وقت التلامس بين المادة المازة والملوثات وتركيز الملوثات الابتدائي ودرجة الحرارة ودرجة الأس الهيدروجيني على أداء هذه المواد. أظهرت الدراسات الحركية أن نموذج Avrami يناسب بدقة النتائج التجريبية لإزالة صبغ CR و CV وبالإضافة إلى الأسبرين بقدرات امتصاص تبلغ 1039 و 1786 و 811 ملجم/جم على التوالي. علاوة على ذلك كشف متساوي حرارة الامتزاز أن نموذج Redlich-Peterson تنبأ بدقة بالبيانات التجريبية لإزالة CR و CV والأسبرين مع قيم معامل التصحيح تساوي الواحد تقريبًا. إضافة إلى ذلك أشارت الدراسات الديناميكية الحرارية إلى الامتزاز الماص للحرارة و التلقائي لعملية إزالة صبغ CR و CV مع قيم موجبة لخصائص ΔS و ΔH بينما أظهر الأسبرين سلوك الامتزاز الطارد للحرارة. هذا البحث تضمن أيضًا نتيجة أخرى مثيرة للاهتمام وهي الثبات العالي وإمكانية تكرار استخدام هذه المركبات النانوية كما يتضح من خلال الانخفاض الصغير في قدرتها على إزالة الملوثات بعد خمس دورات من الامتزاز والامتزاز العكسي. في النهاية يمكننا القول إن نتائج هذا العمل تؤكد أن نماذج الزيقات القائمة على الألومنيوم تمتلك خواص واعدة لإزالة الأصباغ الصناعية والمستحضرات الدوائية من المخلفات المائية الصناعية.

CHAPTER 1

INTRODUCTION

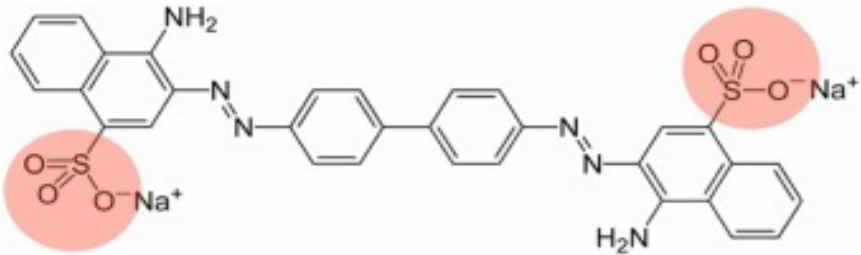
1.1 Background

Globally, the utilization of water has been rising at a rapid rate due to the quick growth of many industries as well as the growth of the human population [1]. Several countries across the world are currently dealing with the issue of water pollution, mainly due to various human activities and the disposal of hazardous elements into the environment. The marine environment is the best for disposing of most of the human and industrial waste [2–4]. This contamination of freshwater sources worsens the water shortage issue, harming public health and ecosystems. According to estimations made by the World Health Organization (WHO), it is predicted that over half of the global population will be facing a water crisis by the year 2025 [5]. These wastes include agricultural-based chemicals, pharmaceuticals, dyes, and personal care products [6]. A significant amount of this pollution comes from industrial sectors, mainly paint, paper, and textile industries, which release wastewater containing many synthetic dyes such as methyl orange, crystal violet, methyl blue, congo red, and others. Many organic dyes are manufactured (annually 0.7 million tons), with around 100 tons are discharged into the environment as effluent [7]. Moreover, pharmaceutical pollutants, a growing group of emerging toxic contaminants, have recently been commonly noticed in varied aquatic ecosystems and soils around the world [8]. Various reasons, such as an increase in annual demand, uncontrolled discharge of

unnecessary medications, and the release of unmetabolized drugs in the drain, have resulted in their accumulation in various water bodies [9]. Although drinking water polluted with pharmaceutical substances for a short period of time has few health risks, long-term contact with such contaminated water in both animals and humans raises significant concerns [10]. Consequently, the elimination of these synthetic dyes and pharmaceutical pollutants from the environment is an essential step in protecting both human health and the ecosystem.

Dyes are categorized as organic pollutants and have been recognized as a worldwide issue due to their extensive release into domestic wastewater, leading to negative impacts on human health [11]. Moreover, due to their complicated nature and unique properties, environmental dyes show limited biodegradability. Therefore, the global concern over the elimination of waste dyes is apparent [12]. Congo Red (CR) is a soluble and stable anionic diazo dye that is widely used in many industries such as textiles, pharmaceuticals, cosmetics, and plastics [13]. CR, containing a reactive azo dye with an azo group in its structure, can be not removed completely by biodegradation. Metabolizing CR results in the production of benzidine, which can have negative impacts on human health. These effects include irritation of the gastrointestinal tract, eyes, and skin, as well as blood coagulation, drowsiness, and respiratory difficulties. Therefore, it is crucial to eliminate CR from the effluent before releasing it into the aquatic system to prevent possible harm to the environment and human health [14].

Table 1: Congo Red dye properties [14].

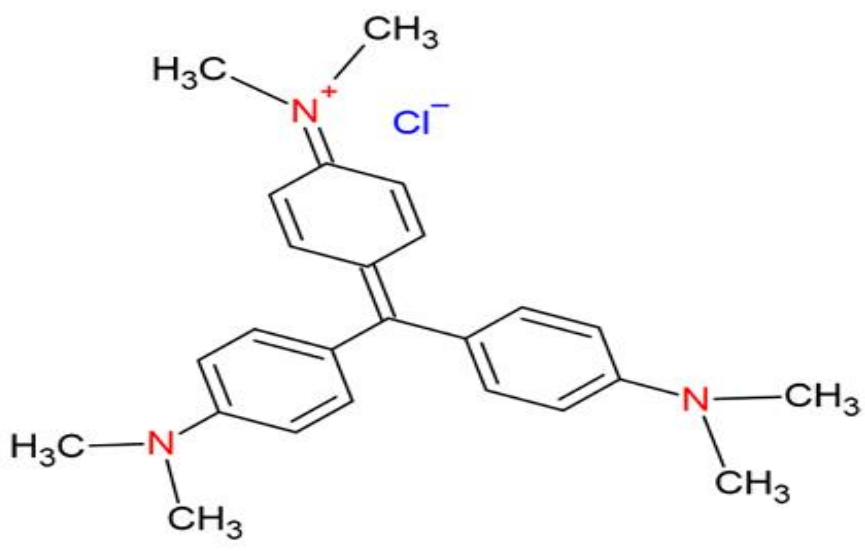
Molecular structure	
Molecular Formula	$C_{32}H_{22}N_6Na_2O_6S_2$
IUPAC name	disodium 4-amino-3-(4-(4-[1-amino-4-sulfonato-naphthalen-2-yl] diazenylphenyl) phenyl) diazenyl-naphthalene-1-sulfonate
Molecular weight	696.66
Maximum wavelength (nm)	497

Crystal violet (CV) is a soluble and stable cationic dye and contains a dimethylamino group attached to each phenyl ring. CV, often referred to as methyl violet and gentian violet, is

widely deployed in various fields such as printing, medical industries, biological systems, and dyeing textiles applications. CV is often used for dyeing various materials, such as nylon, wool, and modified nylon. It is also employed for gasoline, fat, coloring plastics, oil, varnish, and waxes [15]. Despite all these benefits, CV is considered a dangerous biohazard substance due to its harmful impacts on human health. CV is an alkaline toxic substance that has been linked to the irritation of the eyes and corneal damage. Furthermore, ingesting CV has been associated with problems such as diarrhea, vomiting, nausea, respiratory difficulties, and stomach discomfort [15].

Aspirin ($CH_3COOC_6H_4COOH$) is one of the oldest medications used by people and animals to alleviate pain, reduce fever, and decrease inflammation [16]. The IUPAC name of aspirin is 2-acetoxybenzoic acid, with a molecular weight around 180 g/mol. The global yearly use of aspirin is estimated to be over 35,000 metric tons, with approximately one trillion aspirin tablets consumed in the past century. Furthermore, the presence of aspirin has been identified in the aquatic ecosystems of multiple countries. Based on risk assessment studies found in the literature, it has been observed that aspirin has had harmful impacts on the aquatic ecosystem [17]. Aspirin induces oxidative stress, DNA damage, and enzymatic and defective metabolic processes in animals and humans. On the other hand, the fish's levels of toxicity rose as a result of increased exposure to aspirin [18].

Table 2: properties and structure of crystal violet (CV) [19].

Molecular structure	
Molecular Formula	$C_{25}H_{30}N_3Cl$
IUPAC name	(4-(Bis(4-[dimethylamino]phenyl).Methyldiene)cyclohexa-2,5-dien-1-ylidene)-dimethylazanium;chloride
Molecular weight	407.979
Maximum wavelength (nm)	590

Hence, the remediation of synthetic dyes and pharmaceutical contaminants present in wastewater attracts significant attention [19]. Various wastewater treatment approaches, including photocatalytic degradation, biological remediation, and membrane filtration, are used to eliminate these contaminants [2,20]. Nevertheless, these techniques usually demonstrate low efficiency, produce secondary pollutants, and require significant costs. Among all technologies, the adsorption approach has been considered to be a potential technique for treating wastewater since it is cost effective, simple to operate, and could decrease the formation of secondary products [2]. So, developing stable and efficient adsorbents is vital for enhancing the performance of the adsorption approach. Various adsorbent kinds, including metal organic frameworks (MOFs), activated carbon, and graphene oxides (GO), are being utilized to eliminate emerging contaminants, metals, colors, pharmaceuticals, etc.

1.2 Thesis Significance

Based on the literature, zeolitic imidazolate frameworks (ZIFs) adsorbents offer many attractive advantages, like a high surface area, and are widely employed in adsorption approaches. More than 150 ZIF structures have been developed and applied in wastewater remediation applications. However, ZIF materials are difficult to separate from water and expensive to use in water treatment, and their chemical and hydrothermal instability limits their use. Strikingly, metal-based ZIF composites made from higher-valence metals like aluminum (Al) and iron (Fe) solve this issue. In addition, aluminum is an inexpensive and lightweight metal, making it an appropriate option for manufactured aluminum-based ZIFs

as an attractive potential material in the adsorption approach. On the other hand, even with the rapid development of ZIFs for pharmaceutical removal, there haven't been a lot of studies in this area. Therefore, this study will focus on the synthesis of multiple aluminum-based ZIF nanocomposites and their application in the treatment of aqueous solutions encompassing synthetic dyes and pharmaceutical contaminants.

1.3 Thesis Aims

In this work, a novel metal-based ZIF nanocomposite will be synthesized and applied to the adsorptive elimination of some synthetic dyes and pharmaceutical pollutants from synthetic wastewater samples. This thesis aims to achieve the following main objectives:

1. Synthesize nanocomposites using ZIF-8, ZIF-67, and aluminum nanotubes (ANT).
2. Characterize the synthesized nanocomposites via various techniques (e.g., XRD and FTIR).
3. Screen the efficacy of the synthesized nanocomposites in the adsorption process for the removal of various water contaminants.
4. Study the impact of significant operational parameters, such as pH of medium, temperature, contact time, and pollutant concentrations, on the adsorption and removal of water pollutants.
5. Investigate the effectiveness of the prepared nanocomposites during the regeneration process.

CHAPTER 2

LITERATURE REVIEW

2.1 Background

This chapter offers an overview of the zeolitic imidazolate frameworks, their synthesis methods, and their composites for the elimination of water contaminants. Additionally, it offers comprehensive comparisons of the removal of organic dyes and pharmaceutical pollutants by applying ANTs, ZIFs, and their composites. Furthermore, it gives insight into the effects of crucial operational factors like pH, temperature, isotherms, and kinetics studies.

2.2 Zeolitic Imidazolate Frameworks (ZIFs)

ZIFs materials are a kind of metal-organic framework (MOF) that mostly consist of tetrahedrally coordinated transition metals such as zinc and cobalt, together with imidazolate linker [6]. These frameworks are generated by a self-assembly process. The primary reason for the geometric isomorphic behavior between zeolites and imidazolate is the angle of approximately 145° at which the imidazolate bridges the two metals. ZIFs, or zeolitic imidazolate frameworks, contain several desirable properties due to the strong and compact connections between ions of metal and imidazolate [6]. These properties include high crystallinity, a large surface area with tiny pores, rigidity, excellent thermal stability, chemical stability, the capacity to change pore shape, and resistance to water. Moreover,

Significant studies have shown that zeolitic imidazolate frameworks (ZIFs) with the structure of sodalite have the ability to improve the flow of molecules through narrow pores [21]. ZIFs, which combine advantageous attributes of MOFs and zeolites, have potential features for many applications [6]. Fig. 1 demonstrates the variety of advantages in some applications.

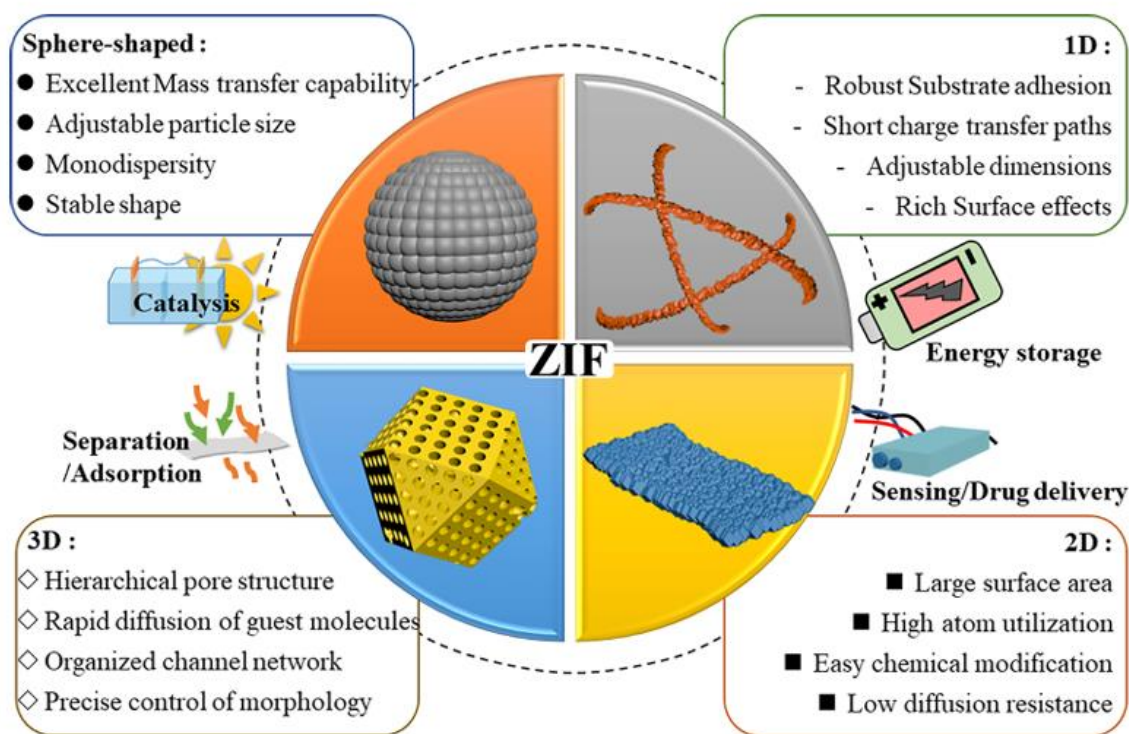


Fig. 1: Advantages of ZIFs with varied dimensions in different applications [22].

One variant of Zeolitic Imidazolate Framework (ZIF), namely ZIF-67, is an isostructural compound that is produced via the bridging of 2-methyleimidazolate anions and cobalt (Co^{+2}) cations [23]. ZIF-67 has a cage-like morphology and plays an essential part in the synthesis of solid and core-shell frameworks. These characteristics allow efficient mass transfer, prevent collapse, and decrease the length of ion dispersal.

These characteristics establish the ZIF as an essential component in the development of electrodes for supercapacitor applications [24]. ZIF67-based materials are utilized in many applications, such as heterogeneous catalytic oxidation processes, hydrogenation-dehydrogenation, esterification, addition reactions, and more. The epoxy-coated nanoporous cobalt-ZIF-67 exhibited excellent anti-corrosion characteristics, as evidenced by an inhibition degree of 81%. Fig. 2 illustrates a structure of ZIF-67. ZIF-8 is a typical geometric structure in the ZIF series, composed of 2-methyleimidazolate anions and zinc (Zn^{+2}) cations [23]. For example, the ZIF-8 nanostructures, produced using the solvothermal approach, include significant features such as a substantial surface area, well-distributed porosity, and the ability to support bimetallic ions. ZIF-8 nanostructures are used as extremely selective and sensitive detectors for detecting nitrogen dioxide gas [6].

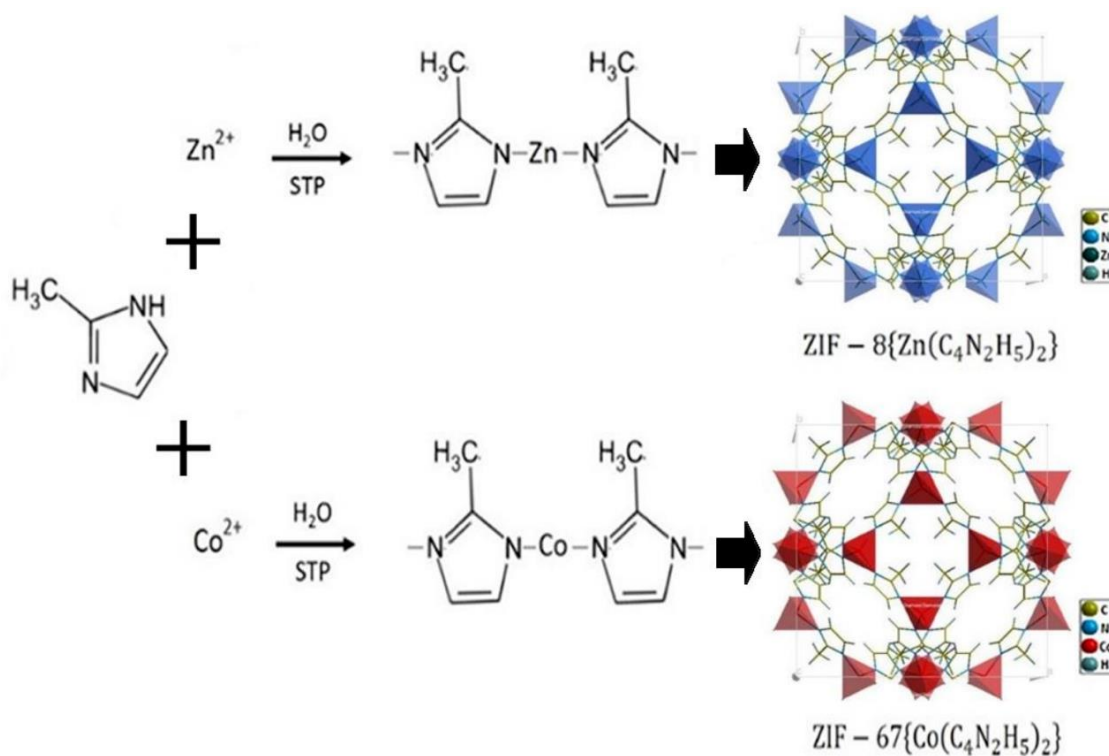


Fig. 2: The structures of ZIF-8 and ZIF-67 [25].

2.3 Synthesis of ZIFs

Several studies have centered on the synthesis of ZIFs in the last decade. In recent years, traditional methods of synthesis using hydro- and solvothermal approaches have been supplemented with additional techniques, including ionothermal, sonochemical, and mechanochemical synthesis.

2.3.1 Solvent-based Synthesis

A solvent-based approach uses water, ethanol, methanol, ammonium, diethyl formamide, and other solvents. Furthermore, depending on which solvent was employed, there were various strategies, such as hydrothermal, solvothermal, sonothermal, microwave, and ionochemical procedures [26].

2.3.1.1 Solvothermal Method

This solvothermal method involves exposing metal and excess ligands to 120 °C for 24 hours in autoclave reactors [26]. This synthesis method was initially used for ZIF synthesis, with Chen's group developing polyhedral crystals using zinc and imidazole linkers within a ratio of 1:2 [27]. Akimbekov et al. later synthesized a series of framework compounds using solvothermal synthesis with various organic solvents [28]. The stability of particles synthesized through solvothermal synthesis was found to be better, with sizes up to 40 nm. Other ZIF materials were also synthesized with similar solvents, but modified synthesis methods using bases such as triethylamine and sodium hydroxide were later used to

increase the reaction rate and yield. Cravillon et al. used methanol and sodium format to try to make ZIF-8 and found that sodium format worked as a deprotonating agent. Moreover, the concentration of ammonium hydroxide was found to affect the morphology and structural features of the synthesized particles [29]. A simple schematic of the solvothermal method is presented in Fig. 3.

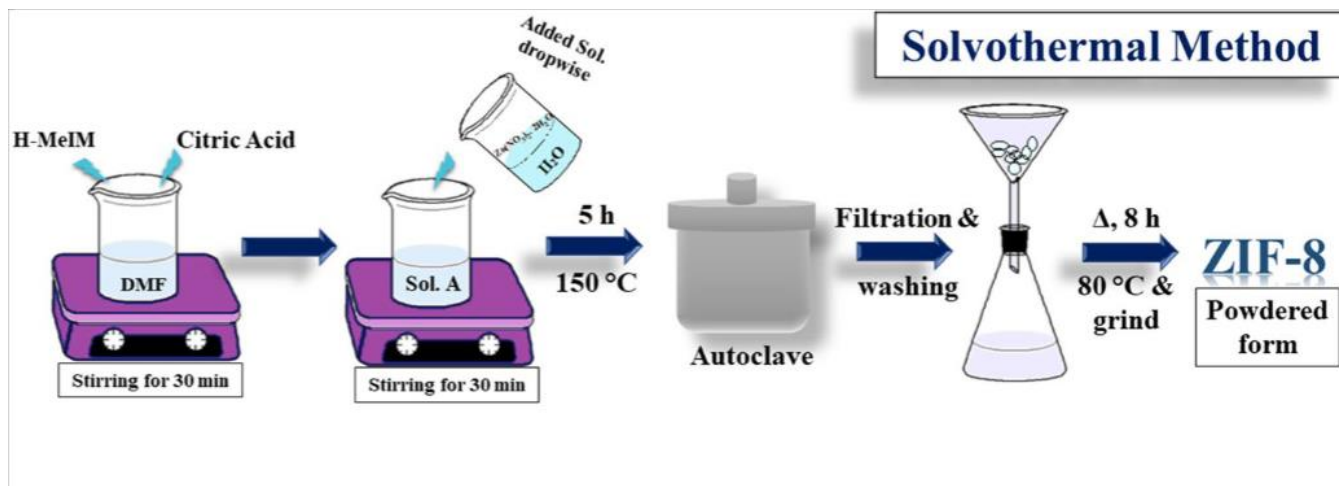


Fig. 3: schematic of pure ZIF-8's solvothermal synthesis [30].

2.3.1.2 Hydrothermal Method

Hydrothermal synthesis method is a chemical reaction that occurs in a closed system with a solvent at high pressure and temperature. This process allows for the production of highly crystalline materials without the need for additional treatments [26]. However, the consumption of organic solvents in the hydrothermal approach is expensive, harmful to human health, and not environmentally friendly. Therefore, researchers are working on developing a more efficient and sustainable method for synthesizing ZIF materials [26]. In one study conducted by Pan et al., nanocrystals of ZIF-8 were successfully synthesized in a pure aqueous medium, yielding higher results in a shorter time compared to organic

solvents [31]. Another study focused on synthesizing ZIF-67 in an aqueous solution, with the particle size varying upon dilution [32]. Modifications were made to the hydrothermal synthesis method, such as the addition of deprotonating agents to decrease the reaction rate and the use of surfactants to reduce the need for solvents and ligands. These surfactants also acted as structure-directing agents, allowing for control over the size and shape of the ZIF crystals. Various parameters, such as surfactant properties and reaction temperature, were found to impact the formation of these zeolitic imidazolate frameworks [33–36].

2.3.1.3 Microwave Method

Microwave method is a modern heating technique that is commonly employed in various chemical syntheses. It is recognized as a convenient, rapid, and inexpensive approach for creating MOF compounds. In comparison to traditional heating methods, microwave irradiation is considered a more environmentally friendly and advantageous method, as it significantly accelerates the reaction rate. This method notably reduces the synthesis time, increases the yield, minimizes the need for ligands, and eliminates the use of deprotonating agents [26,37]. Fig. 4 shows a simple schematic of this approach. In 2016, Butova et al. developed a rapid microwave-assisted hydrothermal technique to synthesize ZIF-8. The method only took 15 minutes and resulted in ZIF-8 with a surface area about $1419\text{ m}^2/\text{g}$ [38].

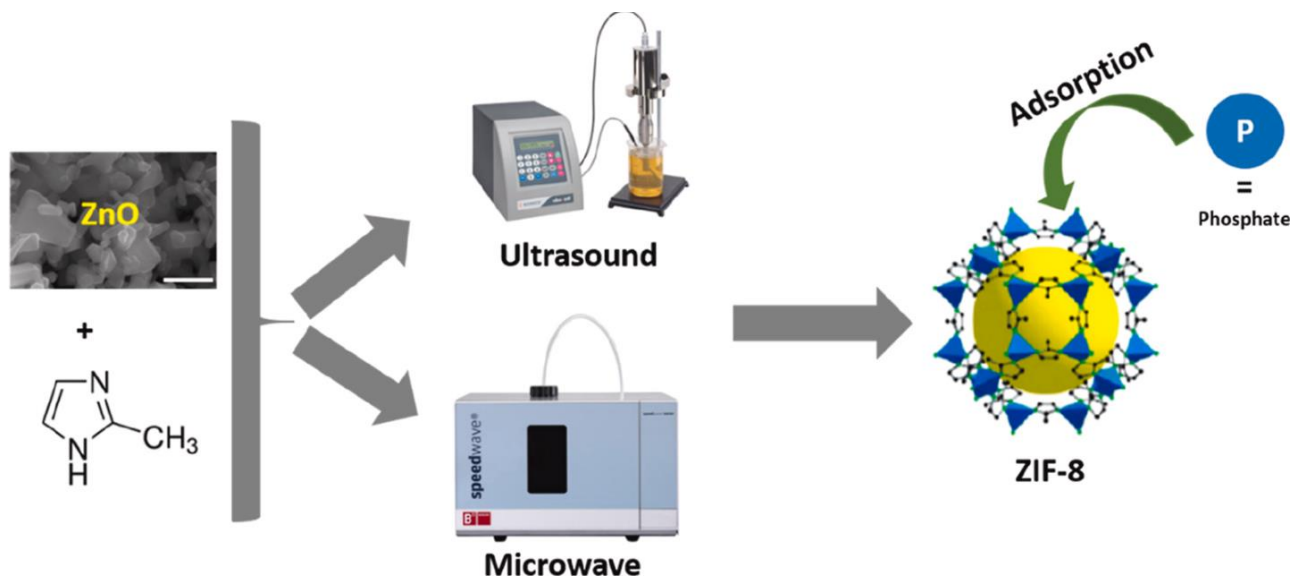


Fig. 4: Microwave synthesis of ZIF-8 [39].

2.3.1.4 Ionothermal Method

The ionothermal method is a novel approach to creating porous materials like ZIF. This method utilizes environmentally friendly ionic fluids and eutectic blends as solvents. Unlike hydrothermal synthesis, ionothermal synthesis could be conducted in an open system because the ionic liquids have low vapor pressure and are nonflammable. ZIF was synthesized by Morrison and his colleagues for the first time by applying an ionic fluid called 1-ethyl-3-methylimidazolium bis-sulfanilamide [40]. Similarly, Yang et al. developed a stable ZIF-8 with a regular shape by applying 1-butyl-3-methyl within a time of 60 min [41].

2.3.1.5 Sonochemical Method

The sonochemical method, in contrast to standard conventional synthesis methods, utilizes ultrasonic waves to generate acoustic cavitations, which promote nucleation and lead to a decrease in crystallization time and a significant reduction in crystal size. Sono crystallization produces smaller crystals with a more consistent size distribution compared to traditional crystallization because of the enhanced nucleation process in the solution [40,41].

2.3.2 Solvent Free Method

A new approach to synthesizing ZIF compounds has been proposed, which involves solventless methods. These methods are considered environmentally friendly and cost-effective alternatives to traditional solvent-based methods. Examples of these methods include the mechano-chemical method, the accelerated ageing synthesis method, and the steam-assisted conversion method [42–44].

2.3.2.1 Steam Assisted Conversion Method

Steam-assisted conversion, or the dry gel conversion, is a technique where amorphous gel powder reacts with vapors of water or amines to create zeolite crystals. Researchers have successfully used this method to synthesize UIO-66, MIL-101 (Cr), MIL-100 (Fe), ZIF-67, and highly porous ZIF-8. This synthesis is advantageous because it does not need the use of acid or salt, is environmentally friendly, avoids hazard solvents, and is cost-effective. Additionally, the synthesized compounds exhibit excellent catalytic activity [45,46].

2.3.2.2 Mechano-Chemical Method

The mechanochemical method is a fast and effective way to synthesize porous materials [47]. In a study comparing mechanochemical within the microwave-assisted approach for synthesizing ZIF at ambient temperature, the mechanochemical synthesis was found to complete the reaction within 30 minutes, while the microwave-assisted method resulted in low conversion after a few hours [48].

2.3.2.3 Accelerated Aging Method

Mottillo et al. introduced a friendly environmental, age-accelerating synthesis for ZIFs that is distinct from traditional-based or free solvent synthesis methods [49]. They proposed a proton transfer mechanism where catalytic salts can induce and speed up the conversion of a metal oxide into a ZIF material [49].

Solvent-free synthesis has become a popular method due to its eco-friendly nature and various advantages. These include fast reaction times, reduced waste and toxic disposal, minimal use of templates, and continuous product formation.

2.3.3 Summary for the synthesis methods of ZIFs

Various approaches for synthesizing ZIFs have been discussed, including solvent-based methods such as solvothermal, hydrothermal, microwave, and ionothermal methods. These methods offer advantages such as high surface area, repeatability, and scalability in a short time. However, they are inefficient due to the excessive use of linkers and solvents. On the

other hand, solvent-free techniques have their own benefits and limitations. These techniques are economical and eliminate the need for solvents.

Table 3: ZIFs adsorbents synthesis methods.

ZIF type	primary material(s)	Method	Temp.	Drying	Ref.
ZIF-8	2.2 mmol zinc nitrate, 8.9 2mmol 2-MIM	Hydrothermal	120 °C	-	[50]
ZIF-67	0.87 g cobalt nitrate, 30 mL methanol, 1.97 g 2-MIM	Solvo-thermal	25 °C	60 °C, air	[51]
ZIF-8	40.2 mmol zinc nitrate, 3.5 2mmol 2-MIM	Sonochemical	30 °C	-	[52]
ZIF-8	0.6 g zinc nitrate, 80 ml methanol, 1.66 g 2-MIM	Sol-gel	25 °C	Freeze-dried, 36 hours	[53]
ZIF-8	39 mmol zinc nitrate, 2-MIM, 80.5 mmol ethanol, aqueous ammonia (25%)	Green solvent s	25 °C	80 °C, 4 hours, vacuum oven	[54]
ZIF-8	mmol zinc nitrate40 mL methanol, 10 mmol 2-MIM	One-step phase inversion method	-	60 °C	[54]

ZIF-67	0.249 g of cobalt nitrate, 25 mL methanol, 0.328 g 2-MIM	-	-	60 °C, 12 hours	[55]
ZIF-67	4 mmol cobalt nitrate, 200 mL ethanol, 16 mmol 2-MIM	Microwave methyod	70-90 °C	100 °C, 24 hours	[56]
ZIF-67	1.50 cobalt nitrate, water, 3.38 kg 2-MIM	-	20 °C	120 °C, 3 days, vacuum	[57]

2.4 Modification of ZIFs

Combining ZIFs with other materials or structures can create composites that are more effective than ZIF alone. Metal oxides and mixed metal oxides have excellent electrochemical, magnetic, and photoelectric properties, making them attractive for creating composites with unique functional properties. Derivatives of ZIFs mixed with metal oxides have been synthesized and investigated for various applications, such as catalysts, separators, adsorbents, microwave-absorbing oxides, storage devices, and sensors. Numerous charge separations and active sites are present on the surfaces of ZIFs, and materials that combine these with other functional materials have found widespread use in various forms and fields [58,59]. These composites demonstrate superior features compared to original substances due to the merging behavior of each functional component. ZIF-8 and ZIF-67 composites have been effectively synthesized applying

various active components like carbon nanotubes, graphene, polymers, polyoxometalates, oxides, metals, and fibers. These composites maintain the individual properties and functions of each part while also overcoming the limitations of individual phases. Compared to pure microporous ZIFs, ZIF-8 and ZIF-67 composite materials not only enhance photocatalytic activity and removal capacity, but they also expand ZIF-8 and ZIF-67's range of applications [60,61].

2.5 Aluminum-based ZIFs

Metal-organic framework (MOF) is a porous material that has been popular in the past two decades. It is a hybrid material, made up of metal nodes or clusters as inorganic parts and organic linkers. As mentioned in the previous section, MOFs have several advantages, including high surface area, pore functionalization, and pore size tunability. Most MOFs are synthesized from divalent cations, such as Zn^{+2} , Cu^{+2} , and Co^{+2} , due to their more controllable crystallization process. However, the chemical and hydrothermal instability of MOF frameworks limit their real application. To synthesize a robust MOF, metals with higher valence, such as aluminum (Al), iron (Fe), and vanadium (V) are preferred to generate metal-based MOFs. Additionally, the stability of MOFs is impacted by their redox activity [62]. Unlike MOFs, aluminum remains unreactive to redox reactions under moderate conditions, and it is comparatively rich on earth compared to other metallic elements. The Earth's crust consists of approximately 8.3 wt.% of aluminum. Moreover, aluminum is both cheap and lightweight, making it highly desirable for the synthesis and use of MOFs on a large scale. Due to these factors, aluminum-based MOF is highly

appealing and adaptable for many industries, such as sensors, gas storage, and adsorbent [62,63] .

Finally, and according to the literature, the aluminum-based ZIFs will have a high potential for use in multi-applications. One of the aims of our research is to synthesis the aluminum nanotube ANTs and use them to produce aluminum-based ZIFs as high-potential adsorbent for removing many pollutants from synthetic wastewater during an adsorption process.

2.6 Chemical and Thermal Properties of ZIFs

2.6.1 Chemical Properties

The development of stable ZIFs under hydrothermal approach has addressed a major limitation of MOFs, making MOF compounds more desirable [58]. Kyo Sung Park and his team conducted a thorough study on the chemical stability of ZIF-11 and ZIF-8 by immersing them in various solvents such as methanol, benzene, sodium hydroxide, and boiling water, at 50 °C for 1–7 days. The samples were observed under a microscope and were noticed to remain inactive in each condition [64].

2.6.2 Thermal Properties

Zeolitic imidazolate frameworks (ZIFs) exhibited reasonable stability at temperatures ranging from 450 to 550 °C when tested employing TGA in an inert atmosphere [56]. Further studies using different characterization techniques revealed that ZIF-8 undergoes partial carbonization above 300 °C in inert and reducing atmospheres, forming an

imidazole-Zn-azirine structure [65]. The degradation of ZIF-8 was noticed to be significant beyond 300 °C at various atmospheres using static TGA. The size of the ZIF molecules and the synthesis conditions were found to be important factors affecting the thermal stability of the particle [64]. Overall, it is suggested that the standard operating temperature for ZIFs was in the 200 °C range at the atmospheric pressure [64].

2.6.3 Surface Area

Porous materials, such as ZIFs, are characterized by their surface area. Smaller particle sizes result in larger surface areas, providing more active binding sites for contaminants. However, sometimes the surface area is low due to incomplete activation of the samples [66]. Various analysis techniques, including N_2 adsorption/desorption and BET analysis, are used to measure the specific surface area, which is recorded in square meters per gram (m^2/g). The highest recorded specific surface area for ZIFs is 2490 m^2/g , while the range varies from 6.050 to 2490 m^2/g [67].

2.7 Removal of Dyes by ZIFs Adsorbents

Organic dyes are a major source of pollution in water solutions, as they are released by various industries. Various industries use these dyes in the production of cosmetics, food, textiles, and other products, leading to the disposal of a large quantity of dyes into wastewater [68]. Adsorbent materials, such as ZIFs (zeolitic imidazolate frameworks) and their composites, have been studied for their ability to remove organic dyes from wastewater. These materials have demonstrated promising results in removing single and multiple dye pollutants. For instance, a composite adsorbent consisting of reduced

graphene oxide and ZIF-67 exhibited exceptional removal efficiency for both anionic and cationic dyes [69]. Another study found that bimetallic ZIFs had enhanced porosity and surface properties, resulting in higher adsorption efficiency [70]. Overall, zeolitic imidazolate frameworks (ZIFs) and their composites have significant potential for treating water and wastewater contaminated with organic dyes.

Recently, in a study executed by Wu et al. [71], the highest uptake capacity of nucleoside/ZIF for CR and MB (cationic dye) reached 769 and 10 mg/g, respectively, which present a 5–6 double in adsorption capacity by ZIF-8 for the same pollutant. Moreover, in the Liu et al. study [72], a composite adsorbent material (ZIF-67-PAA) consisting of polyacrylic acid with ZIF-67 was synthesized using a one-pot synthesis technique. The maximum CV removal by this composite was 1606 mg/g, while ZIF-67 capacity was 1368 mg/g [72]

Table 4: Adsorption capacities of CR and CV dyes onto ZIFs and their composites.

Pollutant	Adsorbent	Adsorption capacity (mg/g)	Ref.
CR	ZIF-8	416	[73]
	ZIF-67	714	[74]
	Fe ₃ O ₄ @Carbon@ZIF- 8	807	[75]
	ZIF-8@CS	922	[76]
	CSM@ZIF-67	538	[77]
	ZFO@ZIF-8	66	[78]
	Zinc titanate@ZIF	96	[79]

	ZIF-67	606	[80]
	ZIF-8	644	[81]
	ZIF-67-PAA	1606	[80]
CV	3D ANF/ZIF-67	199	[82]
	EW@ZIF-8@ PAA	381	[83]
	ZIF-101	7.86	[2]
	ZIF-201	10.83	[2]

2.8 Removal of Pharmaceuticals by ZIFs Adsorbents

Pharmaceutical pollutants, an emerging contaminant, are commonly found in water and sediment globally. They build up in aquatic organisms, posing a significant ecological risk. These residual drugs contribute to the development of drug-resistant microorganisms, which can harm human health through water and food. Consequently, researchers have conducted numerous studies to explore the use of various ZIFs to remove these medical pollutants from water bodies [68]. Capsoni and co-workers synthesized ZIF-8 and applied it to remove ofloxacin antibiotic, achieved adsorption capacity of 95 mg/g [84]. Moreover, the adsorption capacity of tetracycline hydrochloride using ZIF-8 was found to be 56.9 mg/g. In the same study, ZIF-8 and AC@ZIF-8 displayed capacities of 90.7 and 90.5 mg/g for removing tetracycline, respectively. In another research by Ni et al. [85], the capability of ZIF-8 to remove aspirin was investigated, reaching a capacity of approximately 100 mg/g.

Table 5: Adsorption capacities of pharmaceuticals onto ZIFs and their composites.

Pollutant	Adsorbent	Adsorption capacity (mg/g)	Ref.
Aspirin	ZIF-8	100	[85]
Aspirin	ATP@ZIF-8	200	[85]
Aspirin	ATP@ZIF-8-DETA-20	351	[85]
Ceftazidime	ZIF8@SiO2@Fe3O4	151	[86]
Penicillin G	PPI@ SBA-15/ZIF-8	400	[87]
Ofloxacin	ZIF-8	194	[88]
Tetracycline (TC)	ZIF-8	300	[89]
TC	ZIF-8/PAN fibers	885	[90]
TC	Co-ZIF-67 @CNT-700	118	[91]
Norfloxacin	ZIF-8	63	[92]

2.9 Effects of Key adsorption Parameters

2.9.1 pH Effects

The pH of solutions is a crucial element in the adsorption process, especially in the context of dye and pharmaceutical adsorption. The quantity of electrostatic charges in ionized dye

molecules impacts the rate of adsorption in an aqueous solution. [93]. By adjusting the pH with HCl or NaOH solutions, researchers can study the effect of pH on adsorption. Typically, cationic dyes show decreased pollutant removal at low pH and increased removal at high pH. Conversely, anionic dyes exhibit increased dye removal at low pH and decreased removal at high pH. This is because at high pH, the adsorbent surface becomes negatively charged, favoring the adsorption of cationic dyes, and hindering the adsorption of anionic dyes. Conversely, at low pH, the adsorbent surface becomes positively charged, leading to greater adsorption of anionic dyes and reduced adsorption of cationic dyes. Previous studies have shown that the optimal pH for dye removal varies depending on the specific adsorbent and dye class [94]. Thus, in a study conducted Thanh Tu et al. [95], the adsorption capacity of CR by ZIF-67 was reached at around 650 mg/g at a pH of 6, while decreasing with an increase in pH until 510 mg/g at a pH of 12. contrarily, the removal percentage of CV increased from around 58% at pH 3 to 96% at pH 11 [96].

2.9.2 Thermodynamic Studies

Temperature is a helpful indicator for determining the kind of adsorption, which is whether it is exothermic (releasing heat) or endothermic (absorbing heat). If the ability to adsorb increases as the temperature increases, then the adsorption action is classified as endothermic. This effect can be ascribed to the increased motion of the pollutant molecules and the greater number of accessible active sites for adsorption at higher temperatures [97]. The extent of this influence is mostly dictated by the mobility of dye molecules within each specific color category. The reduction in adsorption uptake with rising temperature suggests that the adsorption process is exothermic [94]. The adsorption process can be

characterized by determining thermodynamic parameters such the Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS).

ΔG values dictate the spontaneity of the process. A negative value of the Gibbs free energy change suggests a spontaneous process. The enthalpy change (ΔH) indicates whether a process is exothermic or endothermic and distinguishes between physical and chemical adsorption processes. The ΔS property forecasts the extent of alterations in reversibility, which is influenced by the negative values acquired [98]. For instance, the adsorption of CR dye by ZIF-67 exhibited spontaneous and endothermic behavior with ΔS and ΔH values of 0.31 kJ/mol.k and 78.9 kJ/mol, respectively [23]. Contrarily, the DBPC@ZIF-67 adsorbent with CR demonstrated an exothermic adsorption with $\Delta S = -168.19$ kJ/mol.k and $\Delta H = -60.33$ kJ/mol [99]. Strikingly, the uptake of CV dye by ZIF-8 displayed an endothermic adsorption nature with ΔS and ΔH values of 338.46 kJ/mol.k and 89.899 kJ/mol, respectively [100]. These properties could be collected by the following equations:

Van't Hoff equation:

$$K_d = e^{(-\frac{\Delta H}{TR} + \frac{\Delta S}{R})} \quad (1)$$

Where K_d is the equilibrium constant and R is the universal gas constant ($8.314 \frac{J}{mol.K}$) and.

$$K_d = \frac{q_e}{C_e} \quad (2)$$

The C_e denotes to residual concentration of the pollutant and q_e is an adsorption capacity at equilibrium measured at each temperature. Furthermore, the ΔG at each temperature was estimated using ΔH and ΔS [101]:

$$\Delta G = \Delta H - T \Delta S \quad (3)$$

2.9.3 Kinetic Studies

Adsorption kinetics can be investigated by looking at the rate constant and order of the adsorption process. When selecting an adsorbent material, it is critical to examine the adsorption rate, which should be high and rapid. The examination of adsorption kinetics gives significant insights into the rate of adsorption and provides crucial information for the development of the adsorption system [94]. Accordingly, the impact of contact time between adsorbent and adsorbate was measured at different time intervals, and the results were recorded and presented as kinetic curves. At the first moments, the adsorption rate was significantly high, as there were many unoccupied sites on the surface of the adsorbent [102]. This high adsorption rate is indicated by a slope in the kinetic curve. Moreover, as a system approached equilibrium, the rate of the reaction decelerated until it reached semi-steady state adsorption.

The most common models utilized for analyzing adsorption kinetics are the pseudo-first-order (PFO) and pseudo-second-order (PSO) models. The PFO model assumes that the adsorption rate is proportional to the concentration and is characterized by diffusion through a boundary. However, this model may not accurately estimate the amount of dye adsorbed in all cases. In such situations, the PSO model is used, which is based on the sorption capacity of the solid phase and assumes that chemisorption may be the rate-controlling step in an adsorption process [94].

Table 6: Kinetics models and parameters for fitting adsorption data [94,101,103].

Model	Equation	Parameters
(PFO)	$q_t = q_e \times (1 - e^{-k_1 t})$	$K_1(\frac{1}{min})$: PFO rate constant $q_e(\frac{mg}{g})$: Equilibrium-adsorption capacity
(PSO)	$q_t = \frac{q_e^2 \times K_2 \times t}{1 + q_e \times K_2 \times t}$	$K_2(\frac{g}{mg.min})$: PSO rate constant
Avrami	$q_t = q_e \times (1 - e^{\frac{-(K_v \times t)^{n_v}}{n_v}})$	$n_v(\frac{1}{min^n})$: Avrami model order K_v : Avrami rate constant

Table 7: Comparison of kinetic parameters with those previously reported for CV uptake onto different adsorbents.

Adsorbent	Kinetic Model	$q_e(\text{mg/g})$	K_1 (1/min) K_2 (g/mg.min) $K_a, n(\frac{1}{\text{min}^n})$	R^2	Ref.
ANTs@ZIF-67	Avrami	1786.3	0.0295, 0.7488	0.9973	this study
ZIF-67	Avrami	7068.4	0.0019, 0.8995	0.9939	[80]
M-ZIF-8@ TiO_2	PSO	94.7730	0.0001	0.9677	[104]
ZIF-101	PSO	7.102	0.1909	0.9982	[2]
AGO/Bentonite/LTH	Avrami	649.1	0.034, 0.79	0.994	[105]
M-ZIF-8	PFO	93.5229	0.0063	0.9853	[104]
EY/ZIF-8/CLPAA	PSO	125	0.0001	0.974	[106]
ZIF-102	PSO	7.501	0.2516	0.9957	[2]
S. costatum	PSO	0.12	2.06	0.978	[96]

2.9.4 Isotherm Studies

Isothermic investigations offer valuable insights by elucidating the distribution of adsorbents between the solid and solution phases at sorption equilibrium. The capacity of the adsorbent could be identified by studying equilibrium revisions using adsorption isotherms, which typically represent the ratio of the quantity adsorbed to the remaining quantity in solution at a certain temperature at equilibrium. Several isotherm models were utilized to regress the relevant experimental data. Table 8 lists the nonlinear expressions of

the Langmuir, Freundlich, and Redlich Peterson models. The Langmuir model assumes homogeneous adsorption energy on the adsorbent surface. The foundation of this statement is that monolayer adsorption happens on a surface that is completely homogeneous, with a certain number of identical sites and an unconsidered interaction between the adsorbed molecules. [107]. The Freundlich model is an empirical equation that represents the adsorption of varying affinities at different surface regions. It is hypothesized that the more powerful binding sites are first filled and that the strength of binding decreases as the location becomes more settled. [108]. Otherwise, the Redlich-Peterson model mixes both assumptions (Langmuir and Freundlich) using three parametric empirical equations [101,103].

Table 8: Isotherm models and parameters for fitting adsorption data [101,103].

Model	Equation	Parameters
Langmuir	$q_e = q_{max} \times \frac{C_e \times K_L}{1 + C_e \times K_L}$	q_{max} (mg/g): the maximum adsorption capacity K_L (L/mg): the Langmuir constant C_e (mg/L): the equilibrium concentration.
Freundlich	$q_e = K_F \times C_e^{\frac{1}{n}}$	n: the intensity of adsorption K_F ((mg/g)(L/g)ⁿ): the Freundlich constant
Redlich-Peterson	$q_e = q_{max} \times \frac{C_e \times K_R}{1 + C_e^G \times a_R}$	a_R (L/mg): the Redlich-Peterson constant G: the Redlich-Peterson exponent K_R (L/g): the Redlich-Peterson constant

Table 9: Comparison of q_{max} and isotherm parameters with those previously reported for CV uptake onto different adsorbents.

Adsorbent	Isotherm Model	Parameters			Ref.
ZIF-67	Langmuir	q_{max} (mg/g) = 1368	K_L (L/mg) = 0.132	$R^2 = 0.999$	[80]
	Freundlich	n = 20.2839	K_F ((mg/g)(L/g) ⁿ) = 994.5397	$R^2 = 0.941$	
ZIF-67-PAA	Langmuir	$q_{max} = 1612$	$K_L = 0.554$	$R^2 = 0.999$	[80]
	Freundlich	n = 13.6425	$K_F = 1093.983$	$R^2 = 0.82$	
ZIF-8	Langmuir	$q_{max} = 556.88$	$K_L = 0.1139$	$R^2 = 0.9868$	[104]
	Freundlich	n = 5.3690	$K_F = 191.40$	$R^2 = 0.8868$	
M-ZIF-8	Langmuir	$q_{max} = 835.15$	$K_L = 0.2331$	$R^2 = 0.9835$	[104]
	Freundlich	n = 4.3556	$K_F = 290.61$	$R^2 = 0.8896$	
ZIF-60	Langmuir	$q_{max} = 14250.9$	$K_L = 0.0434$	$R^2 = 0.9756$	[109]
	Freundlich	n = 2.61	$K_F = 1870$	$R^2 = 0.8922$	
	Redlich-Peterson	K_R (L/g) = 516.4 a_R (L/mg) = 0.0168	g = 1.15	$R^2 = 0.9810$	
EY/ZIF-8/CLPAA	Langmuir	$q_{max} = 416$	$K_L = 9.8 \times 10^{11}$	$R^2 = 1.0000$	[106]

	Freundlich	$n = 1.15$	$K_F = 1.21$	$R^2 = 0.8746$	
EW@ZIF-8@PAA aerogel	Langmuir	$q_{max} = 322.6$	$K_L = 0.002$	$R^2 = 0.9986$	[110]
	Freundlich	$n = 1.64$	$K_F = 3.64$	$R^2 = 0.9774$	

2.9.5 Desorption and Reusability

The investigation of the regenerability and reusability of an adsorbent is crucial for its industrial applications, especially when cost is a significant factor. The efficiency of an adsorption approach is enhanced when the adsorbent can be reused [111,112]. Therefore, the recovery of the composites after removing impurities and its ability to maintain its properties after repeated regeneration are important features for industrial use [113]. Different types of ZIF adsorbents have been studied regarding their desorption and reusability. For instance, ZIF-8 showed a 30% decrease in its capacity after three adsorption-desorption cycles [114]. However, NaCl solutions have been employed to revive ZIFs, and high concentrations of NaCl have shown a good regeneration ability [115]. Also, various methods, such as using different eluents and pH variations, have been employed to study the desorption of pollutants from spent ZIFs. Washing of the ZIF adsorbents with eluents like ethanol, NaCl, NaOH, methanol, and HCl increases their ability to be regenerated and reused [116]. Moreover, MRGO/ZIF has demonstrated high performance and stability in terms of recyclability, with a 100% adsorption rate after four cycles [117]. Overall, the reusability and regenerability of adsorbents play a crucial role in

their industrial applications. Some desorption and reusability findings for ZIFs using various adsorbents are summarized in Table 10.

Table 10: Adsorption-desorption studies of multiple ZIF adsorbents.

ZIF type	Pollutant	Eluent	Number Of Cycle	Adsorption Efficiency After N Cycles	Ref.
ZIF-67	CR	Ethanol	5	95 %	[23]
CSM@ZIF-67	CR	NaOH/ethanol	5	90 %	[77]
ZIF-67	CR	Ethanol	3	90 %	[67]
DBPC@ZIF-67	CR	Methanol/DMF	6	81 %	[99]
ZIF-8	CV	Ethanol	3	62 %	[81]
DSAC@ZIF-8	CV	Ethanol	3	90 %	[4]
ZIF-101	CV	Methanol		63 %	[2]
ZIF-201	CV	Methanol		62 %	[2]
ATP@ZIF-8-DETA-20	Aspirin	Sodium hydroxide/methanol	5	84 %	[85]
CTAB-ZIF-67	Diclofenac	NaCl	-	80 %	[115]

CHAPTER 3

MATERIALS AND METHODS

3.1 Background

This chapter provides insight and a summary of the materials that were utilized in this study. Furthermore, this chapter includes details on how we synthesize the adsorbents that were utilized in this research. We thoroughly discussed the preparation methods for ANTs, AIF-8, ZIF-67, ANTs@ZIF-8, and ANTs@ZIF-67. In addition, an overview of the analysis methods used to characterize these adsorbents will be explained, along with the setup and methodology of adsorption experiments.

3.2 Materials

The chemicals employed in this study are crystal violet ($C_{25}H_{30}N_4Cl$) as dye pollutant, 2-methylimidazole (metal-to-linker ratio of 1:4) ($C_4H_6N_2$), Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot H_2O$), Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot H_2O$), aluminum (III) nitrate ($Al(NO_3)_3 \cdot 9H_2O$), urea (CH_4N_2O), ammonium hydroxide solution (NH_4OH), and Sodium Dodecyl Benzene Sulfonate (SDBS) ($CH_3(CH_2)_{11}C_6H_4SO_3Na$). These chemicals have been obtained from Sigma-Aldrich and employed as supplied without purification.

3.3 Synthesis of Alumina Nanotubes (ANTs)

ANTs were synthesized at room temperature by dissolving 32 g of urea with 40 g of aluminum nitrate and 20 g of SDBS in 400 ml of distilled water. The mixture was stirred for 30 minutes at 25 °C before being transferred into a 500-mL autoclave reactor. This mixture inside the autoclave reacted at 120 °C for 20 hours. Then, the mixture was washed five times with distilled water using the centrifuge with the following conditions: time: 10 minutes, and speed: 5000 rpm, to remove the impurities. The drying process of the produced material was conducted in an oven at a temperature of 100 °C before grinding the mixture and obtaining the fine powder product. Finally, the prepared substance underwent a calcination treatment for 3 hours in the muffle furnace at 750 °C.

3.4 Synthesis of ZIF-8

The zeolitic imidazole framework (ZIF-8) was synthesized by dissolving 11.88 g of zinc nitrate in 80 mL of distilled water to prepare a zinc salt aqueous solution. This mixture was added to a second solution prepared from 13.12 g of 2-methyl imidazole and 85 mL of ammonium solution while continuously stirring for 1 hour. After that, the mixture was left to stand for 1 hour, followed by centrifugation at least 5 times (20 minutes each) at 8000 rpm. Washing in between individual runs was done using distilled water. Finally, the collected solids of the ZIF-8 composite have been dried in an oven at 50–70 °C.

3.5 Synthesis of ZIF-67

To synthesize the zeolitic imidazole framework (ZIF-67), a cobalt salt aqueous solution was made by dissolving 11.62 g of cobalt nitrate in 80 mL of distilled water. This solution has been added to a second solution composed of 13.12 g of 2-methyl imidazole and 85 mL of ammonia solution while being stirred continuously for 1 hour. Afterwards, the mixture was left for 1 hour and then underwent centrifugation at least 5 times for 20 minutes each at a speed of 8000 rpm. Purified water was utilized for cleaning in between consecutive operations. Finally, the collected solids of the ZIF-67 adsorbent were dried in an oven at temperatures within the range of 50 to 70 °C.

3.6 Synthesis of ANTs@ZIF-8 nanocomposite

The procedures for preparing ANTs@ZIF-8 secondary nanocomposites involved many steps. First, 11.88 g of zinc nitrate was dissolved in 150 mL of distilled water to prepare a zinc solution. The above zinc solution underwent stirring for 5–10 minutes to dissolve the zinc salt. 0.24 g of ANTs was added to the solution with more stirring. This solution was sonicated at 50% amplitude for 30 min (30 sec on, 3 sec off). In a separate beaker, 13.12 g of 2-methyl imidazole was mixed with about 150 mL of ammonium solution to give the second solution. After that, the second solution quickly poured into the ANTs-zinc salt solution. After completing the addition of both solutions, the mixture has been kept under stirring for about 2 hours. Then, the produced ANTs@ZIF-8 composite was centrifuged five times at 8000 rpm with washing by distilled water between the individual runs. The drying process of the collected solids (ANTs@ZIF-8 composite) was conducted in an oven at 50–70 °C.

3.7 Synthesis of ANTs@ZIF-76 nanocomposite

Regarding the ANTs@ZIF-67 adsorbent, two solutions need to be prepared. The first solution is a cobalt salt aqueous solution, which is made by dissolving 2.91 g of cobalt nitrate in 50 mL of distilled water and stirring for 10 minutes at room temperature to dissolve the cobalt salt. 0.06 g of aluminum nanotube ANTs was weighted, added to the solution, and kept stirring for 10 minutes. This solution was sonicated at 50% amplitude for 30 min (30 sec on, 3 sec off). To prepare a second solution, 3.28 g of 2-methyl imidazole was dissolved in 50 mL of ammonium hydroxide solution. After completing the addition of both solutions, the mixture has been kept under stirring for about 2 hours at room temperature. The mixture was washed with distilled water, using the centrifuge to remove the impurities. Finally, the mixture was dried in an oven at 70 °C before being pulverized into a fine powder.

3.8 Characterization

The developed adsorbents in this study were analyzed to investigate their structure and surface properties using a scanning electron microscope (SEM) combined with energy dispersive spectrometry (EDS). This evaluation assists in studying surface compositions and morphology. Also, Fourier transform infrared (FTIR) spectroscopy within the range of $400\text{--}4000\text{ cm}^{-1}$ was used to analyze the surface functional groups of all manufactured adsorbents. X-ray diffraction (XRD) was used to investigate crystallinity throughout an angle (2θ) of 0 to 80° of ANTs, ZIFs, and their combinations. These analytical approaches provide a helpful understanding of the surface characteristics,

crystallinity, morphology, and surface functional groups of the base and composite adsorbents. BET, or standard multipoint Brunauer-Emmett-Teller technique, was also used to analyze the porous structure of the synthesized adsorbents, including pore volume, pore size, and specific surface area. Likewise, N_2 adsorption and desorption isotherms were measured using the BET technique at a temperature of $-196\text{ }^{\circ}\text{C}$ with an automated adsorption unit. All the above investigations and approaches provided crucial details regarding the porous structure of the adsorbents, pore size distribution, total pore volume, and specific surface area.

3.9 Adsorption experiments

Adsorption experiments were executed to evaluate the efficiency of the selected adsorbent under different conditions. Initially, we started with the screening tests of all bases and composite adsorbents for removing CR, CV, and aspirin pollutants from an aqueous solution. These studies were conducted with standard experimental conditions: an initial pollutant concentration of 100 ppm, a pH of 6.4, an adsorbent dose of 50 mg/L, a shaking rate of 250 rpm, 96 hours of contact time for CR and CV dyes, 45 minutes of contact time for aspirin, and a temperature of $25\text{ }^{\circ}\text{C}$. Following each test, approximately 5 milliliters of each adsorption sample were filtered and analyzed spectroscopically with UV-Vis to measure the remaining contaminant concentrations. The adsorbent that outperformed in a screening test compared with the parent and other composites was selected for further adsorption studies., including examination of the impacts of dye concentration, kinetics, the pH of the adsorption medium, thermodynamic studies, and the reusing of the sorbent.

Adsorption kinetics is an approach that demonstrates the impact of adsorbents and processing mechanisms. Kinetic studies provide essential data for determining the most effective operating parameters in an optimal batch adsorption system. Different models were employed to analyze the kinetics of each nanocomposite and pollutant adsorbate, including the Pseudo first-order, Pseudo second-order, and Avrami models, as shown in Table 7. The process temperature and initial pH of crestal violet solutions were kept at 25 °C and 6.4, respectively, during isotherm studies.

The initial concentrations of CR, CV, and aspirin were changed between 0 and 500 mg/L, with other factors kept constant at room temperature and a pH of 6.4. This allowed for the gathering of adsorption data, which was later utilized to figure out adsorption isotherm parameters using the three adsorption isotherm models: Langmuir, Freundlich, and Redlich-Peterson [7,118]. The Langmuir adsorption isotherm model represents a reversible chemical equilibrium between the adsorbent surface and the adsorbate solution. This model assumes that adsorption takes place at specified and homogeneous spots on the adsorbent surface, with no adsorbate diffusion. The Freundlich isotherm is utilized for heterogeneous surface multiple-layer adsorption with different energies and affinity. It depends on reversible, non-ideal, and monolayer adsorption. Redlich-Peterson is a combination between both models [6].

To further study the effect of temperature and pH on CV, CR, and aspirin adsorption with the chosen adsorbent, the temperature was altered from 10 to 55 °C while retaining a constant pH of 6.4, and the pH was adjusted between 2 and 10 while keeping the temperature constant at 25 °C. Furthermore, five adsorption-desorption cycles were used

to validate the regeneration experiments of the wasted adsorbents. After each iteration, the adsorbent was centrifuged, washed three times with methanol, rinsed several times with distilled water, and dried at 80 °C.

CHAPTER 4

ADSORPTIVE CAPABILITY OF ANTs@ZIF-67 NANOCOMPOSITE FOR THE REMOVAL OF CONGO RED FROM SYNTHETIC WATER

4.1 Background

The presence of congo red (CR) dye in industrial wastewater poses a significant environmental challenge due to its harmful effects on aquatic ecosystems. In response to this issue, adsorption techniques have emerged as efficient and cost-effective methods for CR removal. In this study, a novel nanocomposite was developed by the incorporation of aluminum nanotubes (ANTs) with a zeolitic imidazole framework (ZIF-67) to remove a CR dye from contaminated water bodies. X-ray diffraction, Fourier transform infrared spectroscopy, and Brunauer-Emmett-Teller analysis were performed to investigate the morphology and characterization features of all synthesized adsorbents. The comparison of the developed adsorbent with its parental materials revealed that it outperformed, leading to its selection for further adsorption studies. Accordingly, operating parameters such as initial CR concentration, pH of medium, and temperature were investigated to optimize adsorption efficiency. The optimum CR adsorption capacity by ANTs@ZIF-67 was found to be 1090 mg/g at 25 °C and a pH of 4. The Avrami and Redlich-Peterson models exhibited

well-regressed kinetic and isotherm CR data, indicating a homogeneous adsorption nature. Furthermore, the positive values of thermodynamic properties (ΔH and ΔS) revealed endothermicity and a high level of randomness at the interface. In addition, the reusability investigation highlighted the sustainability and practicality of the ANT@ZIF-67. In summary, the outputs of this work emphasize the potentiality of the ANT@ZIF-67 composites for long-term environmental remediation efforts.

4.2 Characterization

4.2.1 X-Ray Diffraction (XRD) analysis

The X-ray diffraction (XRD) analysis was conducted for ANT, ZIF-67, and their composite (ANT@ZIF-67), and the outcomes are illustrated in Fig. 5. The XRD spectrum of the ZIF-67 sample exhibited many noted peaks at 7.32° , 10.36° , 12.69° , 14.67° , 16.41° , 18° , 19.45° , and 22.1° , corresponding to the (110), (200), (211), (220), (310), (222), (321), and (400) crystal faces. The same peaks reported in the literature confirmed the successful crystallinity formation of the ZIF-67 adsorbent [119]. With respect to the ANT sample, three major bands were observed at 37.88° , 46.09° , and 67.2° , confirming a synthesis of aluminum oxides according to previous studies. These peaks are indexed to the reflections of the (311), (400), and (440) plans, respectively [120,121].

As demonstrated in Fig. 5, the XRD spectra of the ANT@ZIF-67 sample exhibited a similar pattern to ZIF-67, confirming that the crystal structure is still in the developed

composite. Moreover, the small peaks beyond a 2θ angle of 14.67° could be attributed to a weak interaction during the functionalization of ANTs at the ZIF-67 surface.

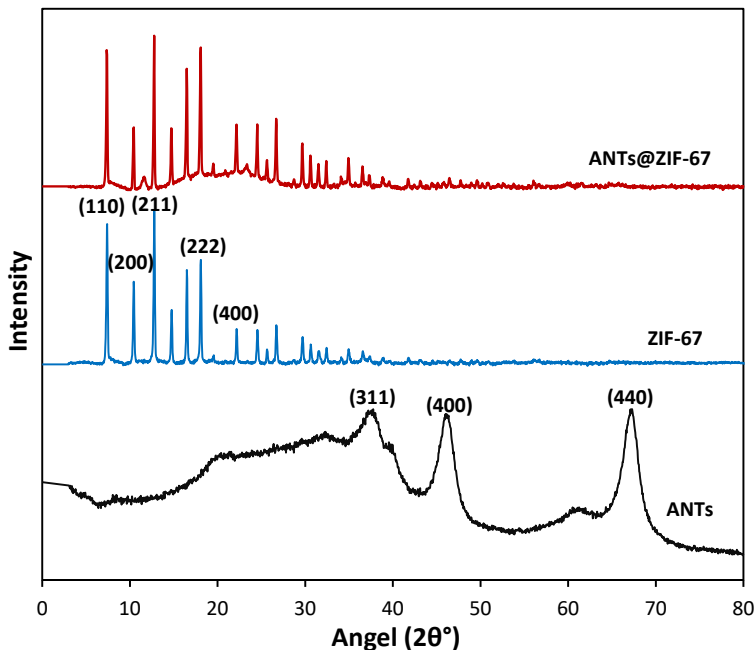


Fig. 5: The XRD pattern of the ANTs, ZIF-67, and ANTs@ZIF-67 adsorbents.

4.2.2 Fourier Transform Infrared (FTIR) spectroscopy analysis.

The FTIR analysis was performed for ANTs, ZIF-67, and ANTs@ZIF-67, and results demonstrated in Fig. 6. The FTIR spectrum of the ZIF-67 demonstrated three major peaks at 425.3 , 1141.5 , and 1566.2 cm^{-1} . The peak at 425.3 cm^{-1} associated with the Co-N bond, while all remaining peaks were similar to 2- methylimidazole peaks, in agreement with previous reports [122,123]. Accordingly, 1141.5 and 1566.2 cm^{-1} corresponded to the aromatic C-N and C=N bonds. Moreover, the other bands below 800 cm^{-1} and between 900 and 1400 cm^{-1} related with the in and out bending of ring plane [122,123].

In the spectrum of ANTs, a main peak was clearly observed at 510.3 cm^{-1} , associating with Al-O, according to the literature. In addition, there were three minor bands around 1097.9 , 1635.8 , and 3397.2 cm^{-1} related to the Al-OH, H-O-H, and O-H vibration bonds, respectively [120]. Strikingly, the incorporation of ANTs with ZIF-67 displayed a similar spectrum. All major peaks of ZIF-67 were exhibited in the ANTs@ZIF-67, confirming the presence of the Zn-N, Co-N, C-N, and C=N bonds in the developed composite. Furthermore, the Al-O band clearly vanished in the ANTs@ZIF-67 sample, which could be explained by the small weight percentage of aluminum tubes in a developed composite.

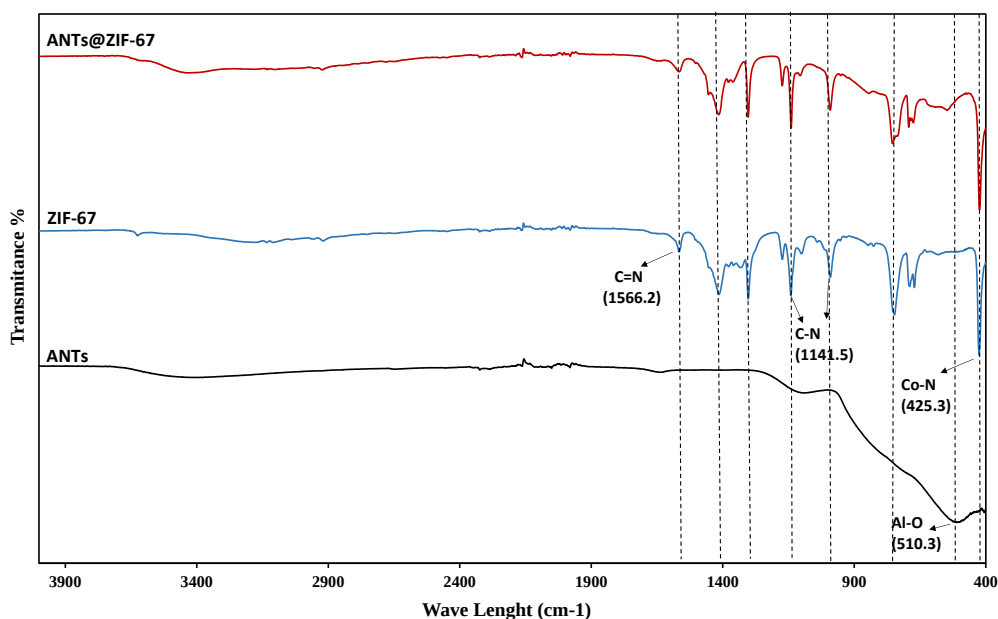


Fig. 6: FTIR spectra of ANTs, ZIF-67, and ANTs@ZIF-67 adsorbents.

4.2.3 Brunauer-Emmett Teller (BET) analysis

Fig. 7 illustrates the nitrogen adsorption-desorption isotherms of aluminum nanotubes, ZIF-67, and ANTs@ZIF-67 nanocomposite. The isotherm obtained from the ANTs sample is type IV, which indicates capillary condensation based on the IUPAC classification. The

ANTs sample exhibited an initial sudden rise in adsorption value at low pressure, revealing the existence of micropores, and a gradual increase in N_2 uptake as a relative pressure increase. Moreover, beyond 40% of relative pressures, the isotherm pattern displayed observed hysteresis, pointing to the mesopores and reversible capillary condensation on the adsorbent surface [124]. These findings match many previous studies in the literature [124–127].

The N_2 isotherm of the ZIF-67 displayed a large adsorption at low relative pressures, confirming the category I isotherm and indicating the microstructure nature of the material. Additionally, a small hysteresis of the ZIF-67 sample suggested the presence of tiny mesopores in its crystalline structure, in agreement with the previous reports [128–131]. As seen in Fig. 7, the ANTs@ZIF-67 nanocomposite has conserved the behavior of the parent ZIF, illustrating a type I isotherm also, but with a smaller N_2 amount, which can be attributed to the partial functionalization of the ANT particles within the pores of ZIF-67.

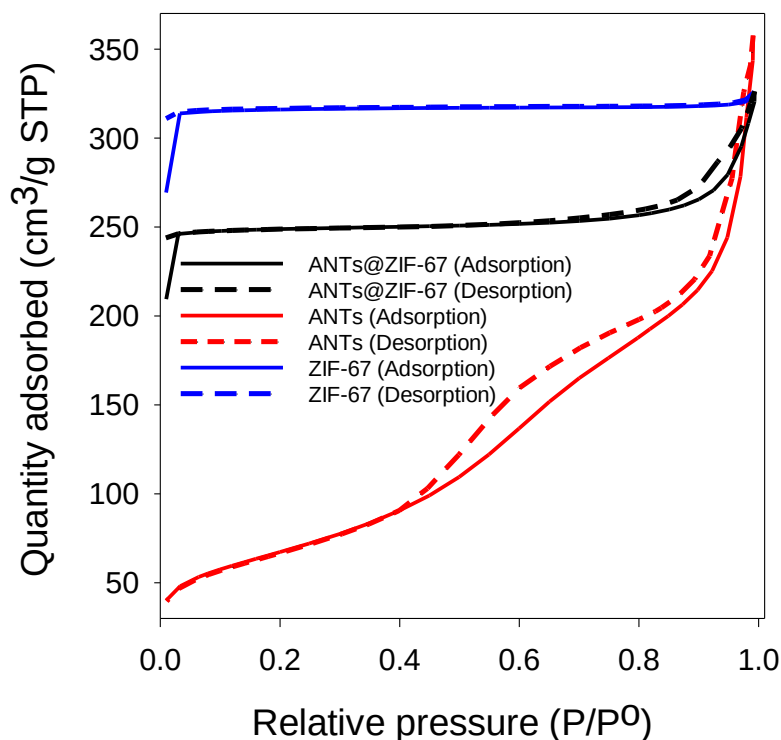


Fig. 7: Isotherm of N₂ adsorption on and desorption from ANTs@ZIF-67 nanocomposite and its parental materials (i.e., ANTs and ZIF-67)

Table 11 presents a summary of the textural features such as the BET surface area (S_{BET}), Langmuir specific surface area, specific pore volume (V_p), and pore size (d_p) of the ANTs, ZIF-67, and ANTs@ZIF-67 composite. The ZIF-67 adsorbent exhibited a high BET surface area of $1158.2 \text{ m}^2/\text{g}$ and a low pore size of 1.71 nm . The ANTs sample had a low surface area ($S_{\text{BET}} = 273.55 \text{ m}^2/\text{g}$) and a total pore volume of $0.565 \text{ cm}^3/\text{g}$. As expected, the ANTs@ZIF-67 nanocomposites had a smaller surface area than the bare ZIF-67 sample (S_{BET} of $912.8 \text{ m}^2/\text{g}$).

Table 11: Textural properties of ANTs, ZIF-67, and ANTs@ZIF-67 nanocomposites.

Adsorbent	S_{BET} (m^2/g)	Langmuir Specific Surface Area (m^2/g)	V_{P} (cm^3/g)	d_{P} (nm)
ANTs	237.5	348.3	0.565	7.25
ZIF-67	1158.2	1382.1	0.020	1.71
ANTs@ZIF-67	912.8	1090.1	0.130	2.00

4.2.4 Scanning Electron Microscopy (SEM) and Energy Dispersive

Spectrometry (EDS) analysis

The ANTs, ZIF-67, and ANTs@ZIF-67 samples were imaged using scanning electron microscopy (SEM), and the results are displayed in Figs. 8a–c. Accordingly, Fig. 8a exhibits the SEM image of ANTs. The obvious nanotubes in the agglomerate structures were noted, which is in accordance with the literature [132]. The EDX analysis of ANTs demonstrates the presence of AL and O elements, verifying their formation. Furthermore, ZIF-67's morphology demonstrated polyhedral structures, as shown in Fig. 8b. This sample displays a distinct rhombic dodecahedron crystal shape e, which is in line with ZIF-67 synthesized by the autoclaved method [133–135]. Fig. 8c shows an SEM image of ANTs@ZIF-67 within a blending between paternal particles. Therefore, the success of functionalizing aluminum nanotubes on the ZIF surface was confirmed, which could explain the outperformance of ANTs@ZIF-67 in the screening tests.

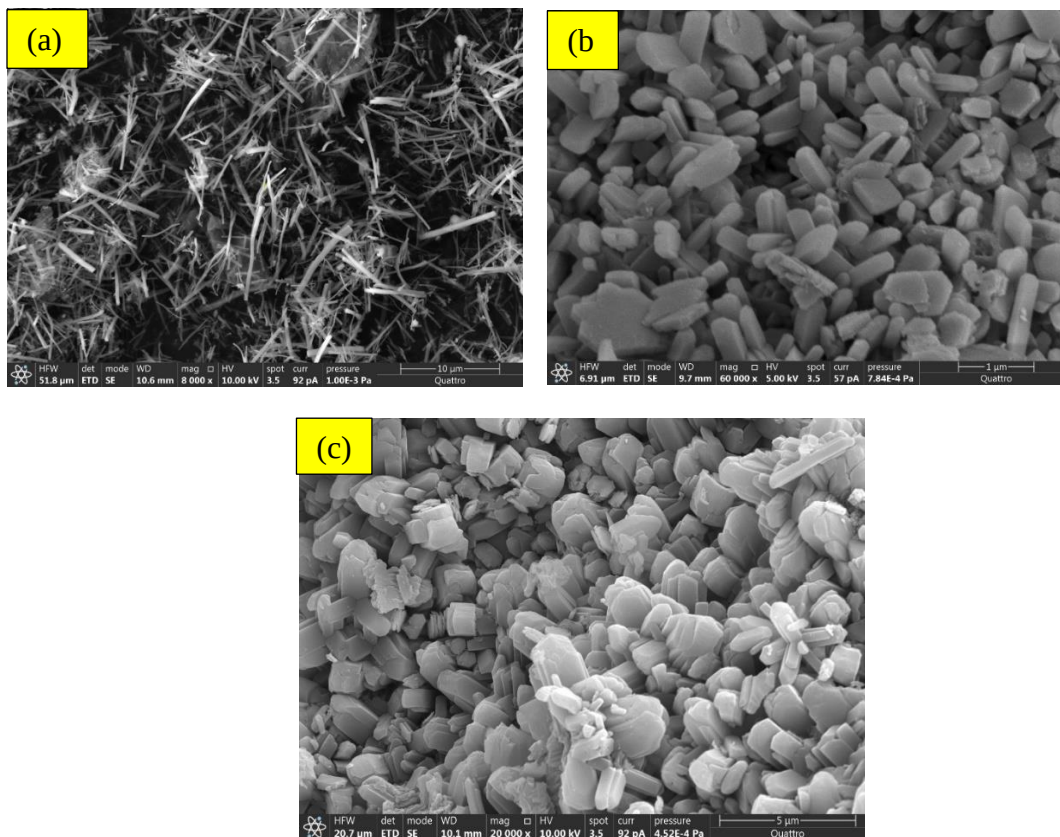


Fig. 8: SEM images of a) ANTs, b) ZIF-67, and (c) ANTs@ZIF-67.

On the other hand, the elemental compositional analysis of the ANTs@ZIF-67 nanocomposite was performed to ensure the incorporation between the ANTs and ZIF-67 materials. As can be observed in Table 12, the developed composite was comprised of C, N, Co, AL, and O. The outcome demonstrated that the composite was successfully synthesized without any impurities.

Table 12: Elemental analysis of ANTs, ZIF-67, and ANTs@ZIF-67.

Element wt.% / Adsorbent	ANTs (This study)	ANTs@ZIF-67 (This study)	ZIF-67 [135]
C	-	38.5	44.1
N	-	22.9	34.4
Co	-	22	22.3
AL	38.1	2.9	-
O	69.9	13.8	3.3

4.3 Adsorbent screening

In the realm of wastewater treatment, the identification and optimization of effective adsorbents play a pivotal role in addressing environmental pollution challenges. In this study, we conducted a comprehensive adsorbent screening to evaluate the efficacy of aluminum nanotubes based on ZIF composites in removing congo red from aqueous solutions. As mentioned in an introduction, the capacity of CR on ZIF-8 and ZIF-67 was 176 and 250 mg/g, respectively, according to a study by Nguyen et al. [136] and Zhao et al. [77].

Recently, Metal-based (MOFs) and their composites have emerged as a common adsorptive material for removal pollutants from aqueous solutions. In this research, ANTs were applied to target the elimination of CR. The outcomes shown in Fig. 9 indicate that ANTs exhibit a low removal capacity, reaching 81.2 mg/g. On the other hand, ZIF-67 has been described as an effective sorbent for removing adsorbates from water-based solutions.

For example, Zhao et al. [77] investigated the adsorption capacity of CR on CSM@ZIF-67 at 350 mg/g. Additionally, Zhang et al. [23] compared the adsorption of MB, MR, MO, and CR on ZIF-67 individually, recording that the removal of CR exceeded 90%, while that of MO was 80%, with the removal of MB and MR being relatively low. Hence, in this work, ZIF-67 has been selected for CR removal due to its potential properties. As illustrated in Fig. 9, ZIF-67 showed an uptake of 217.1 mg/g. To enhance the adsorbent efficacy, a secondary composite adsorbent (ANTs@ZIF-67) was synthesized and applied in screening tests. Accordingly, the ANTs@ZIF-67 composite demonstrated a capacity of 519.5 mg/g for removing CR, while the ANTs exhibited a capacity of 81.2 mg/g.

Motivated by the special efficacy observed in ANTs@ZIF-67 in comparison to its base elements, ANTs and ZIF-67, the performance of this secondary composite is better than that of these bases by approximately 400% and 240%, respectively. We have selected it for deeper investigation in the following sections, that will focus on aspects like CR concentration, contact time, temperature, pH, and regenerability.

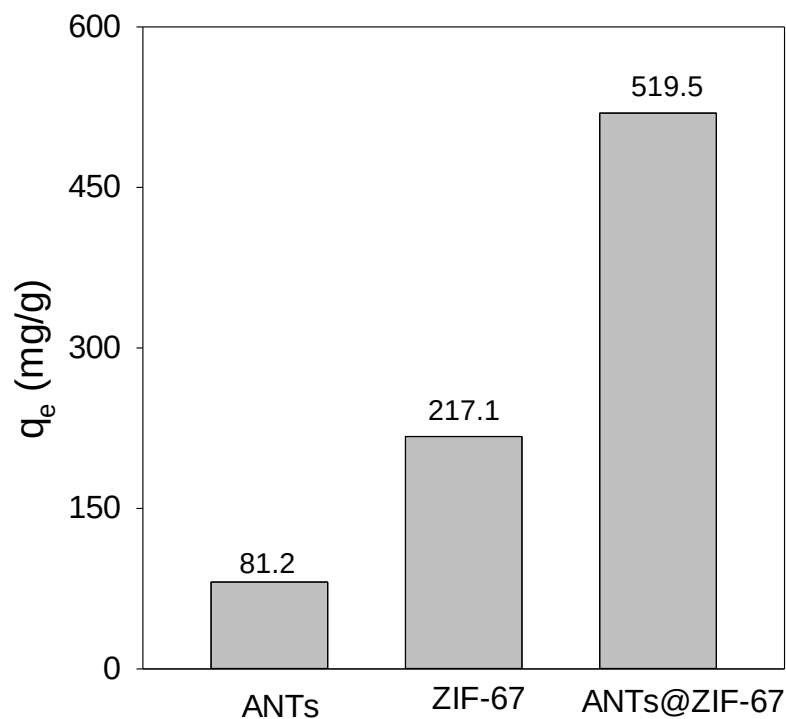


Fig. 9: Adsorption screening of CR on the ANTs, ZIF-67, and ANTs@ZIF-67. The screening experiments were done with conditions: CR concentration = 100 ppm, pH = 6.4, temperature = 25 °C, time = 96 hours, and dose = 50 mg/L.

4.4 pH Effect

The pH of congo red solutions was varied from 4 to 10 to study the effects of pH on CR elimination. The experiments were performed at 25 °C, with an initial dye concentration of 100 ppm (mg/L) and a dosage of 50 mg/L. After 96 hours of CR adsorption, the remaining concentration was measured, and results demonstrated in Fig. 10. Accordingly, the downward trend was clearly observed within the pH window of 4 to 10. The ANTs@ZIF-67 nanocomposite exhibited maximum dye uptake at 4 pH, achieving a capacity of 1090 mg/g. The composite performance decreased with increasing pH, reaching 825 and 504 mg/g at 5 and 6 pH, respectively. This trend continued in the same manner until pH 10, with a relative low adsorption capacity of 296 mg/g. For instance, Yanzho

Feng et al. investigated the removal of CR by DBPC@ZIF-67, which was 450 mg/g at a pH of 4 and around 225 mg/g at a pH of 10 [99].

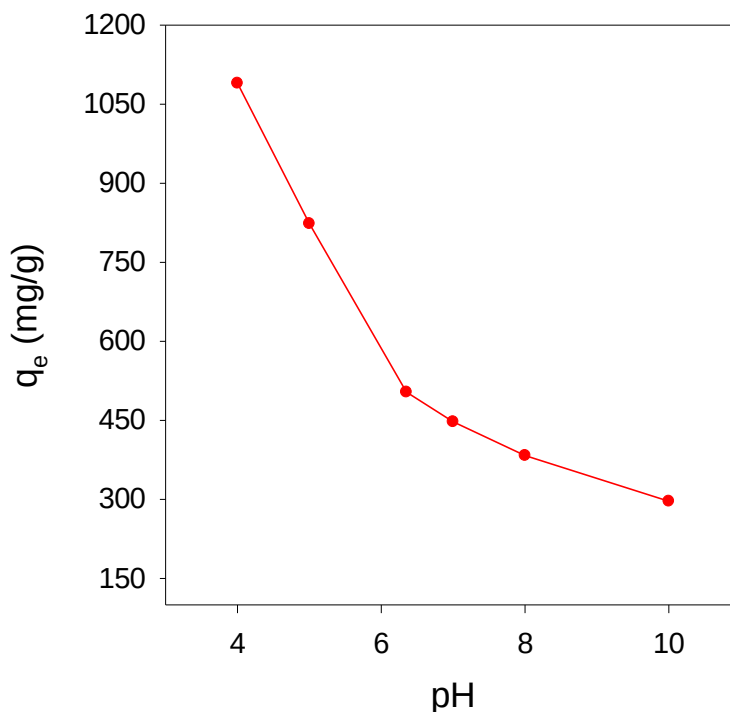


Fig. 10: pH effects on CR adsorption onto the ANTs@ZIF-67 nanocomposite. The pH experiments were done with conditions: CR concentration = 100 ppm, temperature = 25 °C, time = 96 hours, and dose = 50 mg/L.

In terms of charges, congo red is an azo anionic dye with PK_a value of 4.1, and usually demonstrates a negative charge [137]. Moreover, ZIFs and their combination with earth metals frequently demonstrate a high PH_{PZC} and typically have a positive net surface charge at acidic and neutral pH levels [67]. Based on this, the appropriate adsorption mechanism of CR onto ANTs@ZIF-67 nanocomposite is an electrostatic interaction. The high performance at pH 4 could be attributed to the strong relative positive charge of the ZIF composite, leading to more electrostatic interaction with a negative dye at this pH level. Similar findings of CR adsorption are found in the literature [138–140].

4.5 Adsorption kinetics

The adsorption dynamics research described the solute adsorption rate on the adsorbent surface [141]. As a result, we adjusted the contact time between a CR adsorbate and an ANTs@ZIF-67 adsorbent from 5 minutes to 120 hours until we reached equilibrium. The kinetic experiments were executed at room temperature and a 100-ppm initial CV concentration, while the pH and dosage were kept consistent at 6.4 and 50 mg/L, respectively. Accordingly, the kinetic obtained was regressed and applied to several kinetic models, like the PFO, PSO, and Avrami models. The experimental and predicted kinetic data are presented in Fig. 11 and Table 13.

As displayed in Fig. 11, The CR adsorption onto ANTs@ZIF-67 achieved equilibrium after 96 hours. The Avrami model exhibited the best fit of experimental data, with an R^2 value of 0.993. Moreover, PFO and PSO showed a weak representation of the data with R^2 values of 0.83 and 0.89, respectively. The PFO model depicted a maximum removal capacity of 481.7 mg/g, and PSO predicted 508.9 mg/g, compared with the experiment value of 505.3 mg/g. These findings indicated that both chemisorption and physisorption are significant factors in the adsorption process, matching many reports in the literature [56,77,142,143]. According to Jiang et al. [142], the kinetic studies of CR removal by ZIF-8 were examined, and equilibrium was achieved after 12 hours with an uptake capacity of 400 mg/g. In the study conducted by Zhang et al. [23], the removal of MO and CR by ZIF-67 was examined and reached equilibrium approximately at 2 hours for MO and half an hour for CR.

Table 13: Predicted kinetic parameters of congo re dye adsorption onto ANT@ZIF-67 nanocomposite.

Kinetic Model	Parameters	
PFO	$q_e(\text{mg/g})$	481.7
	$K_1 \text{ (1/min)}$	0.1758
	R^2	0.8324
PSO	$q_e(\text{mg/g})$	508.9
	$K_2 \text{ (g/mg.min)}$	0.0006
	R^2	0.8910
Avrami	$q_e(\text{mg/g})$	1039.0
	K_a	7.0284×10^{-5}
	$n(\frac{1}{\min^n})$	0.3043
	R^2	0.9930

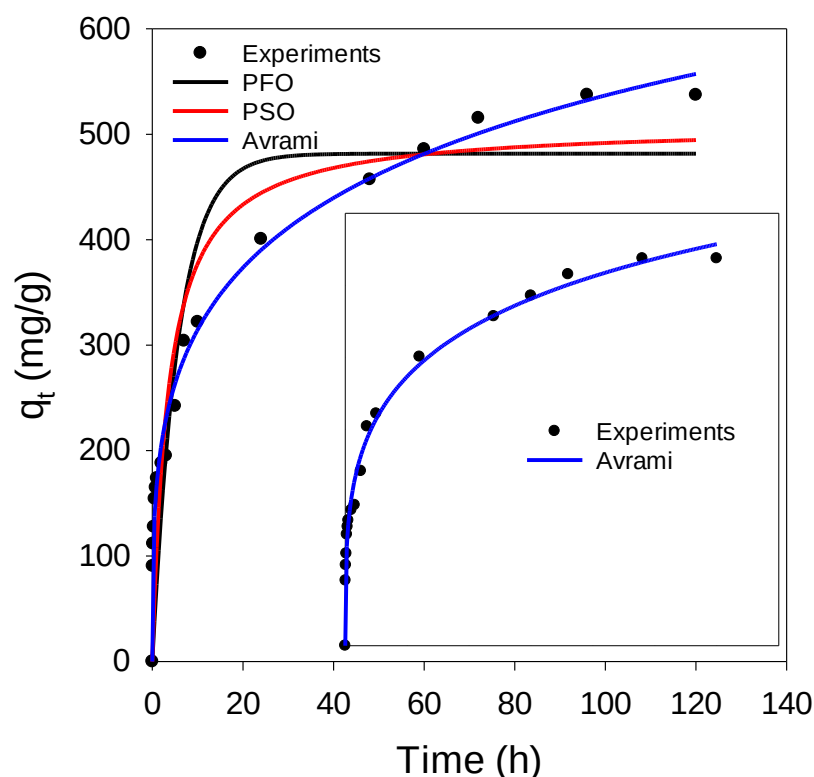


Fig. 11: Adsorption isotherm models of CR onto ANTs@ZIF-67 nanocomposite. The kinetic experiments were done with conditions: CR concentration = 100 ppm, pH = 6.4, temperature = 25 °C, and dose = 50 mg/L.

4.6 Adsorption isotherms

To perform the isotherm studies, we conducted serial adsorption experiments with different initial dye concentrations while maintaining all other conditions constant. Then, three non-linear isotherm models (Langmuir, Freundlich, and Redlich-Peterson) were employed to regress these experimental data. Fig. 12 displays the adsorption isotherms of congo red on ANTs@ZIF-67 in single dye systems, and Table 14 presents the calculated model parameters. According to Fig. 12, the Redlich-Peterson model displayed excellent symmetry with the experiment data, demonstrating an R^2 value of 0.9928. Furthermore,

the Langmuir isotherm model exhibited an acceptable representation of data with an R^2 value of 0.9832. The maximum removal capacity predicted by the Langmuir equation was 1169 mg/g. These findings matched those previously reported for CR dye adsorption [23,56,144,145]. Contrarily, the Freundlich model failed to regress the data, as revealed by the low R^2 value (0.8840). On top of that, the dimensionless Redlich-Peterson constant ($g = 0.9928$) was close to unity, meaning that the Redlich-Peterson model is closer to the Langmuir than the Freundlich model, which depicts a homogeneous adsorption nature.

Table 14: Parameters of the isotherm models.

Model	Parameters	
Langmuir	q_{max} (mg/g)	1169
	K_L (L/mg)	0.0276
	R^2	0.9832
Freundlich	n	3.07
	K_F ((mg/g)(L/g) ⁿ):	163.6
	R^2	0.8840
Redlich-Peterson	K_R (L/g)	23.63
	a_R (L/mg)	0.0066
	g	1.2027
	R^2	0.9928

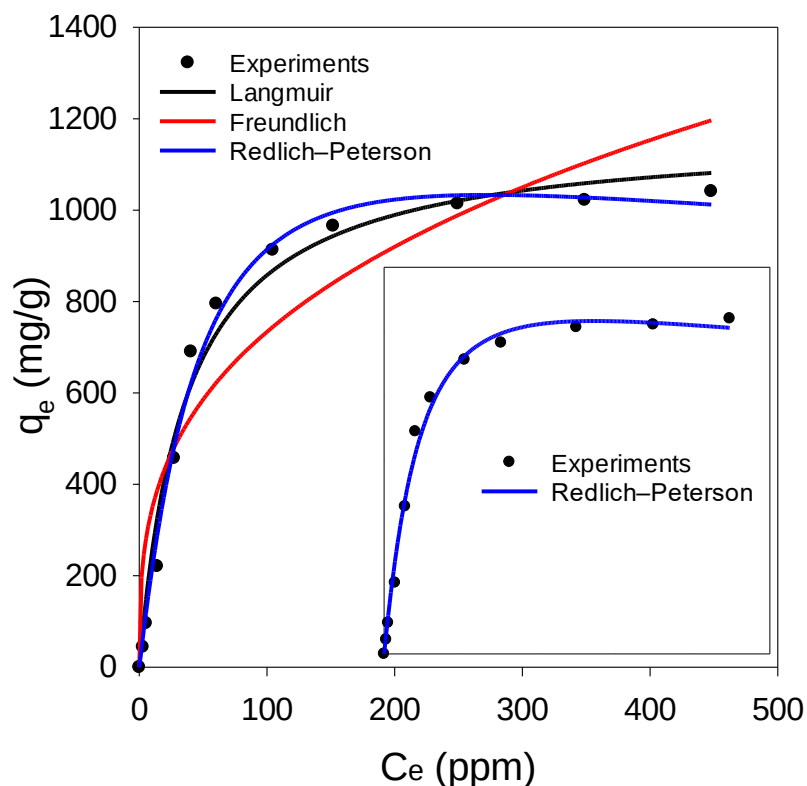


Fig. 12: regression of isotherm data of CR adsorption onto the ANT@ZIF-67 nanocomposite.

4.7 Thermodynamic study

The temperature-effect investigation of CR adsorption was executed at 10, 25, 40, and 55 °C, while keeping other conditions constant. The thermodynamic properties such as the enthalpy change (ΔH), Gibbs free energy (ΔG), and entropy change (ΔS) can be calculated by applying the equations 1-3 [146–148]. The extracted thermodynamic properties of congo red removal by ANT@ZIF-67 are presented in Table 15.

As seen in Fig. 13, the equilibrium capacity increased with the increase in temperature, which suggests that the CR adsorption process is endothermic. At a temperature of 55 °C, the uptake reached 664 mg/g, compared with 421 mg/g at 55 °C. The positive value of ΔH

(10.4 kJ/mol) confirmed this endothermic nature [149,150]. Moreover, the positivity of the ΔS change indicated a high level of randomness at the interface. The change in ΔG within the range of -3.94 to -6.22 kJ/mol reflects that spontaneous physical adsorption has a main contribution to CR removal [151]. Jiang et al. also recorded the same phenomenon by applying ZIF-8 to remove CR from an aqueous solution [142].

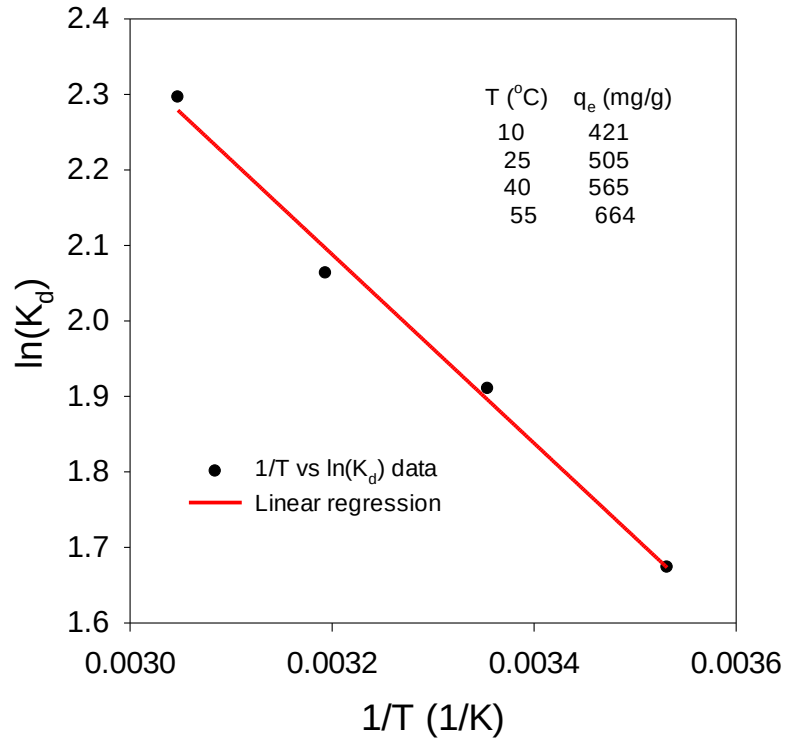


Fig. 13: Plot of the Van't Hoff equation in the range of 10-55 °C. The experiments were done with conditions: CR concentration = 100 ppm, pH = 6.4, time = 96 hours, and dose = 50 mg/L.

Table 15: Thermodynamic properties of CR adsorption onto the ANTs@ZIF-67 nanocomposite.

T (°C)	T (K)	$\Delta G (\frac{KJ}{mol})$	$\Delta H (\frac{KJ}{mol})$	$\Delta S (\frac{J}{mol.k})$
10	283	-3.94	10.40	50.64
25	298	-4.70		
40	313	-5.46		
55	328	-6.22		

4.8 Comparison of ANTs@ZIF-67 with Other Adsorbents

The maximum adsorption capacity of CR on the ANTs@ZIF-67 composite in this study was 1090 mg/g at pH of 4 and 100 ppm initial CR concentration, which is a potential value compared with many other adsorbents. Table 16 summarizes the CR adsorption capacities of multiple adsorbents, as reported in many previous studies.

Table 16: CR removal capacity on a multiple adsorbent.

Adsorbent	Adsorption capacity (mg/g)	Ref.
ANTs@ZIF-67	1090	This study
ZIF-67	714.3	[152]
ZIF-9@SMM	146	[145]
Bentonite	35.84	[153]
CSM@ZIF-67	538.4	[77]
Commercial activated carbon	168	[154]
Bael shell carbon	98.04	[155]
polyacrolein	51.8	[156]

4.9 Reusability of the ANTs@ZIF-67 nanocomposite

Adsorption and desorption tests were done to see how stable and recoverable the ANTs@ZIF-67 composite adsorbent was. The dose of ANT@ZIF-67 used was 2 g/L. The adsorption-desorption tests were conducted five times using a CR solution with a 5 mg/L (ppm) concentration at room temperature and a pH of 6.4. Following each adsorption process, the composite was washed using a methanol solution, then dried in an oven at 65 °C for future use. Outcomes are displayed in Fig. 14. The initial adsorption process achieved a removal efficacy of 100%; likewise, the second and third adsorption processes also showed a high removal efficacy of 99.65%. In the same manner, the fourth and fifth cycles still provided a high percentage of removal above 99%, which led us to conclude that the adsorption and desorption processes of ANTs@ZIF-67 with the CR system happened smoothly and showed an excellent result.

After five cycles, the removal performance stayed over 99%, indicating the adsorbent's excellent stability. Additionally, the adsorbent which is a solid metal-based composite material can be easily separated from the dye solution, offering another important advantage in applicability. Finally, these results confirmed the superior recoverability and stability of the ANTs@ZIF-67 composite as an adsorbent.

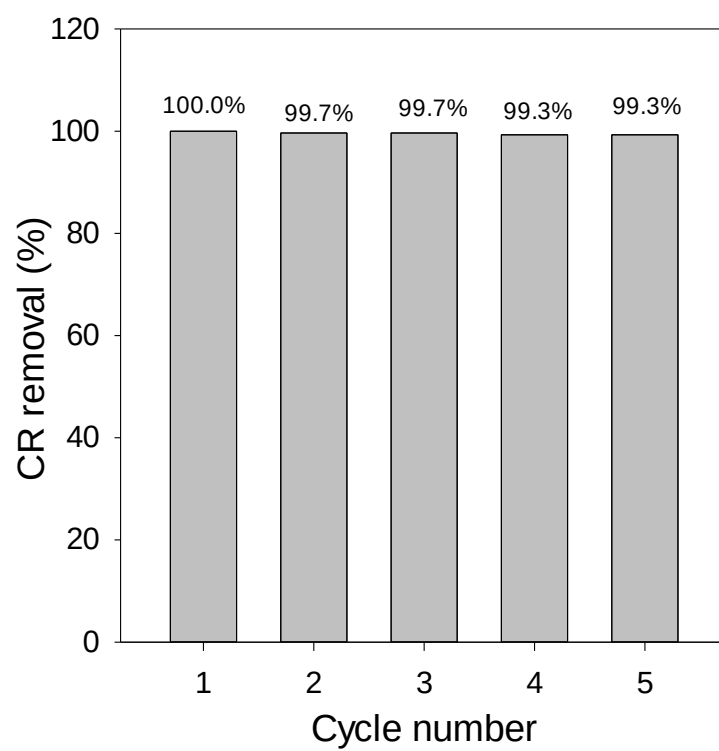


Fig. 14: Reusability of the ANTs@ZIF-67 nanocomposite.

CHAPTER 5

ADSORPTIVE CAPABILITY OF ANT_s@ZIF-8

NANOCOMPOSITE FOR THE REMOVAL OF ASPIRIN

FROM SYNTHETIC WATER

5.2 Background

The disposal of pharmaceutical pollutants into the environment has harmful damages on both human health and the aquatic ecosystem. In this study, a novel adsorbent (composed of aluminum nanotubes and a zeolitic imidazolate framework) was synthesized, characterized, and applied to remove a hazardous medical water pollutant (aspirin). The adsorption performance of the developed ANT_s@ZIF-8 was benchmarked against its parental materials. The findings reveal that aspirin's adsorption capacity onto the nanocomposite is 808.9 mg/g, which is higher than its adsorption on ANT_s and ZIF-8 individually. The textural properties, morphology, functional groups, and crystallinity were investigated by Brunauer-Emmett Teller, Fourier transform infrared spectroscopy, and X-ray diffraction. The present study investigated the impact of contact time, initial aspirin concentration, temperature, and pH on the adsorptive elimination of aspirin by the ANT_s@ZIF-8 nanocomposite. The Redlich-Peterson and Avrami models exhibited the best fit of adsorption isotherm and kinetic data with R^2 of 0.9932 and 0.9987, respectively.

Thermodynamic results indicated the exothermicity, spontaneity, and physical nature of the aspirin adsorption process. Furthermore, regeneration studies demonstrated a minor reduction in aspirin removal with ANTs@ZIF-8 nanocomposite, confirming its reusability. Overall, the results of this work reveal a promising adsorbent (ANTs@ZIF-8) for efficient pharmaceutical removal from contaminated water bodies.

5.2 Characterization

5.2.1 X-Ray Diffraction (XRD) analysis

To investigate the crystalline features and phases of the developed adsorbents, X-ray diffraction (XRD) testing was conducted on the samples. Fig. 15 displays the pattern of ANTs, ZIF-8, and ANTs@ZIF-8. Based on the XRD results, ANTs were observed to have three prominent peaks at 37.88° , 46.09° , and 67.2° , which corresponded to the (311), (400), and (440) planes, respectively. These peaks are associated with aluminum oxides, and they align with the findings reported in other studies [120,126]. On the other hand, the XRD pattern of ZIF-8 exhibits multiple peaks at 2θ angles of 7.33° , 10.38° , 12.72° , 14.69° , 16.44° , 18.02° , 19.48° , 22.11° , and 24.48° . These peaks corresponded to the crystallographic planes (110), (200), (211), (220), (310), (222), (321), (411), and (332), respectively. The findings are consistent with previous reports, confirming ZIF-8 crystals with high crystallinity have been successfully prepared [157–161]. According to Fig. 15, the modified ANTs@ZIF-8, which was created, has comparable peaks to the original ZIF-8, suggesting that the crystal structure was maintained after nanocomposite formation [157]. However, a few diffraction peaks exhibited a little shift towards the lower 2θ angles,

suggesting a slight expansion of the ZIF-8 crystallinity. This effect might be attributed to ZIF-8 framework deformation produced by repulsive interactions between the ANTs and imidazole groups. Conversely, the pattern related to ANTs clearly vanished in the composite, which could be explained by a weak interaction with ZIF-8.

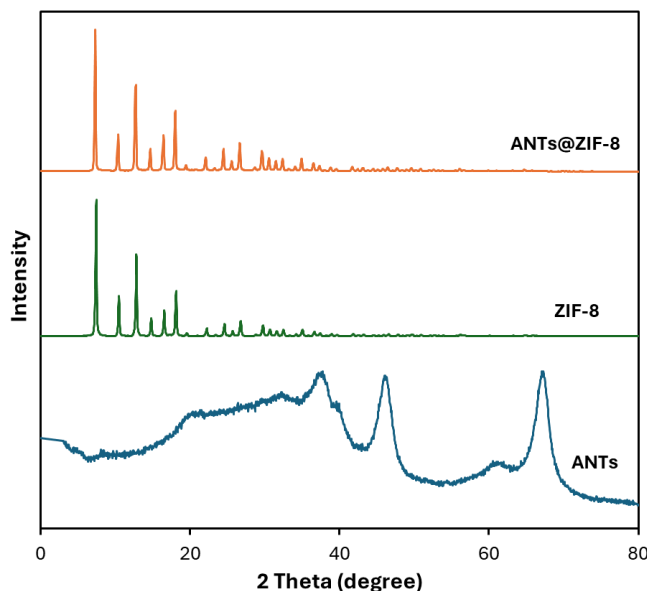


Fig. 15: XRD spectra of ANTs, ZIF-8, and ANTs@ZIF-8 nanocomposite.

5.2.2 Fourier Transform Infrared (FTIR) spectroscopy analysis

Fig. 16 illustrates the FTIR spectra ($4000\text{--}400\text{ cm}^{-1}$) of the base and composite adsorbents that were synthesized in this study. The FTIR spectrum of ANTs displays a pronounced peak at 510 cm^{-1} , indicating the Al-O bonds [120,126,162]. Furthermore, three peaks at 3397 , 1635 , and 1097 cm^{-1} were observed. The peak at 1097 cm^{-1} corresponds to the Al-O-H bond, while the peaks at 1635 and 3397 cm^{-1} are associated with the H-O-H bond and the hydroxyl vibrational bond (OH), respectively [120].

The FTIR spectra of the ZIF-8 sample had distinct peaks at 420, 648, 693, 758, 953, 993, 1145, 1179, 1309, 1417, 1581, 2927, and 3139 cm^{-1} , as shown in Fig.16. These FTIR bands matched those already reported in literature[157–160,163]. The major peak near 420 cm^{-1} represents Zn-N stretching vibration, which indicated a chemically combined reaction between zinc and 2-methylimidazole [158,160]. The absorption peaks around 648 and 693 cm^{-1} ascribed to the bending of the imidazole ring in an out-of-plane manner, whereas the range of 1309-1417 cm^{-1} is reflective of the stretching of the entire the ring [158,160]. The peaks at 953, 993, 1145, and 1179 cm^{-1} correspond to the aromatic C-N bending mode, while the peak at 758 cm^{-1} is related to the C–H bending vibration [160]. Moreover, the signal around 1581 cm^{-1} arose from the C=N stretch vibration [160]. The bands at 2927 and 3139 cm^{-1} , respectively are consistent with the aliphatic and aromatic C-H stretching modes [159,163]. As displayed in Fig. 16, all signals, including the tree main peaks (Zn-N, C-N, and C=N), that appeared in ZIF-8 could still be found in ANTs@ZIF-8, indicating the presence of ZIF-8 on the developed composite. Contrarily, The AL-O band from ANTs was clearly Faded in ANTs@ZIF-8, indicating that no significant chemical interactions between aluminum particles and ZIF-8.

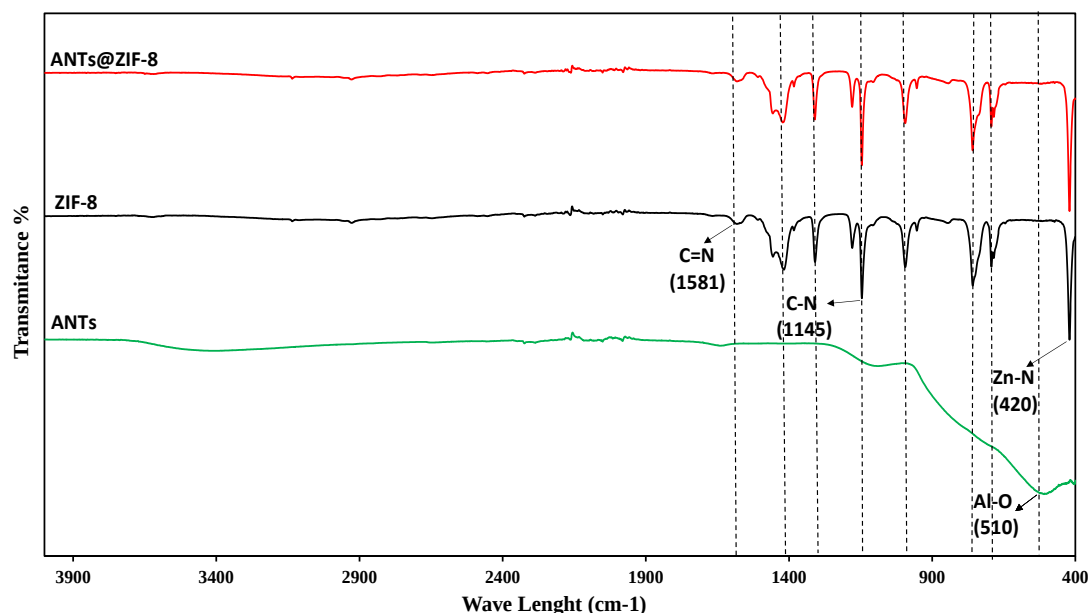


Fig. 16: FTIR spectra of the synthesized adsorbents (ANTs, ZIF-8, and ANT@ZIF-8).

5.2.3 Brunauer-Emmett Teller (BET) analysis

To determine the pore size and surface area of the developed adsorbents, a BET analysis was conducted, including the nitrogen adsorption and desorption isotherms as illustrated in Fig. 17. Based on the IUPAC physisorption isotherm classification, ANT has an IV isotherm between the H1 and H2 hysteresis loops within the relative pressure range of 0.42–0.9. These outcomes indicate the presence of a mesoporous structure, which is in line with those reported previously [125–127]. The evident sharp slop (closer to H2) at extremely low relative pressure could be attributed to the existence of extra micro-porosity in the ANT sample [127]. Furthermore, the H1 isotherm is related to capillary condensation in pore channels, which might involve channel adjustments [124].

Moreover, the ZIF-8 sample exhibits the typical type I isotherms, indicating the microstructure nature of the ZIF-8, as clearly shown in Fig. 17. Moreover, a very small

hysteresis was observed in the ZIF-8 sample, suggesting the existence of tiny mesopores in its crystalline structure. Similar findings have been reported in previous studies [130,159,160]. For ANTs@ZIF-8 nanocomposite, adsorption/desorption isotherm type I is also seen, which confirms the presence of ZIF-8 micropore structure.

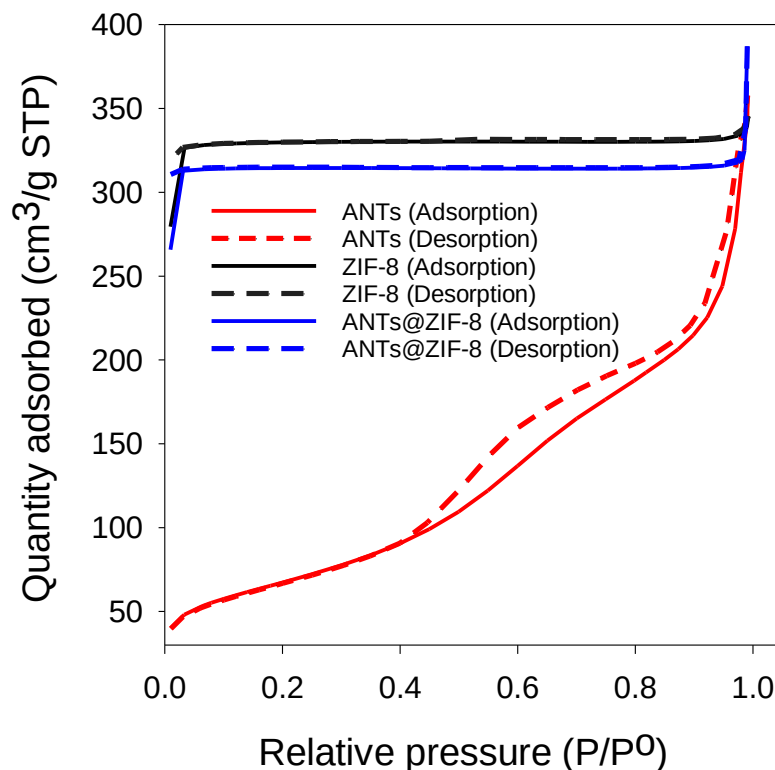


Fig. 17: Isotherm of N_2 adsorption on and desorption from ANTs, ZIF-8, and ANTs@ZIF-8 nanocomposite.

Table 17 presents a comprehensive summary of the textural characteristics, including the specific surface area (S_{BET}), Langmuir specific surface area, specific pore volume (V_p), and pore size (d_p) of the ANTs, ZIF-8, and their composite. The S_{BET} of the parent materials, namely ANTs and ZIF-8, are 237.5 and 1209 m^2/g , respectively, with corresponding pore sizes of 7.25 and 1.71 nm. Regarding the ANTs@ZIF-8 composite, the

BET surface area slightly decreased (approximately 4.4%) compared with ZIF-8 values, while the pore size was still almost the same. The results obtained from this investigation were compared with the previously reported findings, as shown in Table 17.

Table 17: Textural properties of ANTs, ZIF-8, and ANTs@ZIF-8 nanocomposites.

Adsorbent	S_{BET} (m^2/g)	Langmuir Specific Surface Area (m^2/g)	V_p (cm^3/g)	d_p (nm)	Ref.
ANTs	237.5	348.3	0.565	7.25	This study
ZIF-8	1209.0	1442.0	0.028	1.71	This study
ANTs@ZIF-8	1155.4	1373.6	0.114	1.7	This study
ZIF-8	1144.7	-	0.5	1.56	[159]
ZIF-8	1228	1896	0.5850	-	[160]
Commercial γ - Al_2O_3	215	-	1.23	11.9	[127]
gamma Al_2O_3	247.9	-	-	-	[125]

5.2.4 Scanning Electron Microscopy (SEM) and Energy Dispersive

Spectrometry (EDS) analysis

Fig. 18a-c displays the SEM images of ANTs, ZIF-8, and ANTs@ZIF-8 samples synthesized in this study. The SEM image in Fig. 18a demonstrates aggregated nanotubes of aluminum oxides, confirming the synthesis of ANTs. In addition, the elemental diffraction X-ray spectroscopy (EDS) indicated that the ANTs sample comprised AL and O elements. These findings matched previous ones in the literature [132,164]. The

morphology of the ZIF-8 sample exhibited a consistent smooth rhombic dodecahedral shape, as illustrated in Fig.18b [165]. Similar structures were previously described by Jin et al. and Fu et al. [166,167]. Moreover, Fig. 18c clearly demonstrates the effective modification of aluminum nanotubes on ZIF-8. The morphology of the ANTs@ZIF-8 nanocomposite remained mostly unchanged when compared to ZIF-8. This suggests that the functionalization included did not cause any significant harm to ZIF-8's structure.

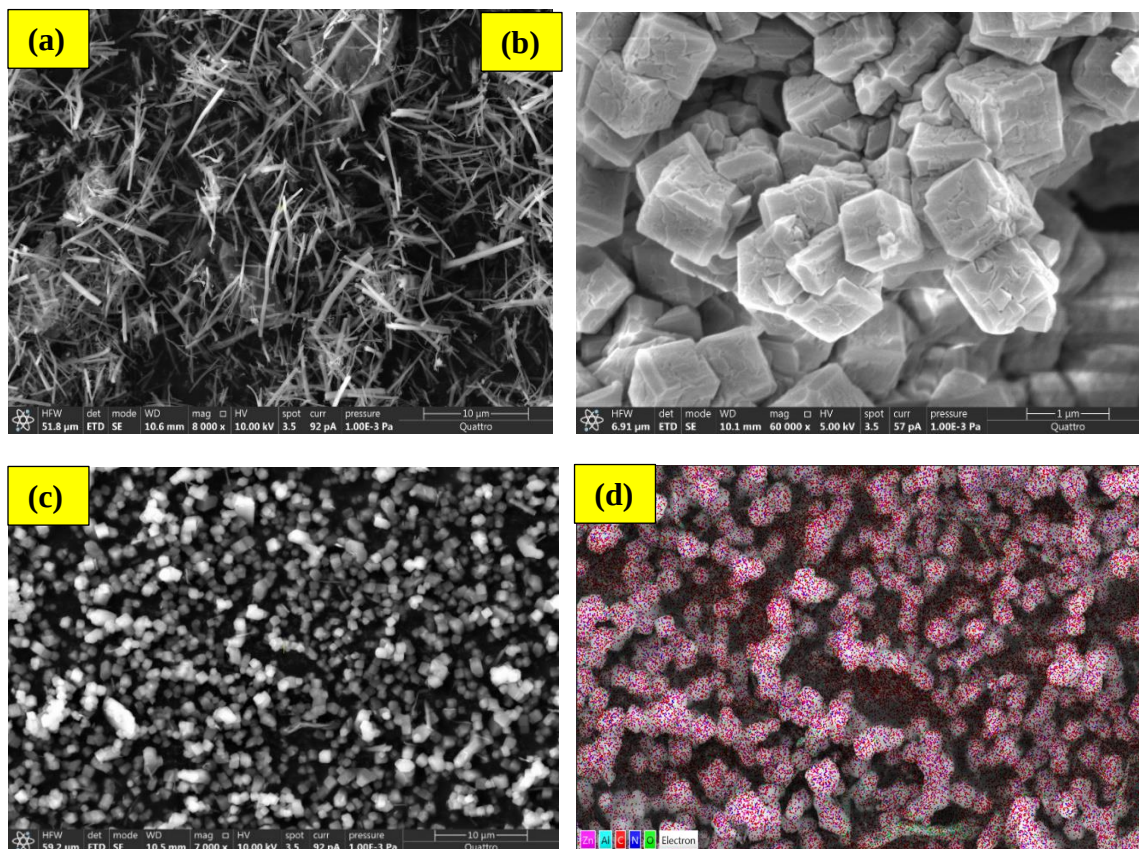


Fig. 18: SEM images of (a) ANTs, (b) ZIF-8, (c) ANTs@ZIF-8, and (d) elemental mapping of ANTs@ZIF-8.

From an elemental composition point of view, the purity of the ANTs@ZIF-8 adsorbent was further confirmed by EDX analysis. The elemental mapping of this nanocomposite

revealed a uniform distribution of Zn, N, C, AL, and O elements in its shape (Fig. 18d).

Table 18 displays the composition (by weight) of all samples.

Table 18: Elemental analysis of ANTs, ZIF-8, and ANTs@ZIF-8.

Element wt.% / Adsorbent	ANTs (This study)	ANTs@ZIF-8 (This study)	ZIF-8 [157]
C	-	44.2	57.9
N	-	30.8	26.1
Zn	-	20.5	16.0
AL	38.1	0.7	-
O	69.9	3.8	-

5.3 Adsorbent screening

As mentioned in the introduction, extensive study has been centered on employing MOFs and ZIFs for efficient adsorption of pharmaceutical contaminants in water. For instance, in research executed by Wu et al. [168], the adsorption of tetracycline (TC) on ZIF-8 was examined, reaching an adsorption capacity of 930 mg/g. In another study by Ni et al. [85], the ability of ZIF-8 to remove aspirin was examined, with a resulting capacity of approximately 100 mg/g. These studies indicate that the adsorption efficiency of ZIF-8 is

unsatisfactory and requires more improvement. To enhance the adsorption performance of ZIFs, functionalization of the metals on ZIF to produce metal-based ZIF adsorbent is an attractive approach used in much recent research. According to Ni et al. [85], the efficacy of ATP@ZIF-8 is double that of ZIF-8 in the removal of aspirin pollutants, with capacities around 200 and 100 mg/g, respectively. Among those results, Fankang Zhao et al. [169] investigated the adsorption of tetracycline (TC) and diclofenac sodium (DF) on Fe_3O_4 @MOF-525, which achieved an adsorption capacities of 277 and 745 mg/g, respectively.

With a growing worldwide interest in protecting the environment using eco-friendly materials and developing effective remediation methods, a lot of studies have been performed on the application of MOFs and ZIF materials for the uptake of various pharmaceutical water contaminants. For instance, Nasri et al. [2] investigated the adsorption capacity of CV on ZIF-101 and ZIF-201 at 7.86 and 10.83 mg/g, respectively. Likewise, the ZIF-67 and ZIF-8 capacities of CV were 6.82 and 6.5 mg/g, respectively, with an adsorbent dose of 50 mg [2]. In this study, aluminum nanotubes (ANTs) were synthesized and functionalized on ZIF-8 to develop novel nanocomposite adsorbents. These composites underwent a comprehensive screening test to evaluate their efficacy in the removal of aspirin as a medicine pollutant model, as shown in Fig. 19. All experiments were done with the standard conditions: temperature = 25 °C, pH = 6.4, an initial aspirin concentration of 100 mg/L, time = 45 minutes, and dose = 50 mg/L.

As demonstrated in Fig. 19, the base substances ANTs and ZIF-8 depicted adsorption capacities of 71.1 mg/g and 711 mg/g, respectively. To enhance the efficacy of these base adsorbents, the composite ANTs@ZIF-8 was synthesized. Thus, the secondary composite

ANTs@ZIF-8 achieves an adsorption capacity of 808.9 mg/g, which is higher than the capacity of its base.

Thus, the performance of ANTs at ZIF-8 adsorbent represents 1.14 of that of ZIF-8 and doubles ten times that of ANTs. This outstanding performance of the ANTs@ZIF-8 nanocomposite makes it the preferred choice for further study in later sections, which will examine some essential parameters such as contact time, pH, temperature, initial pollutant concentration, and reusability.

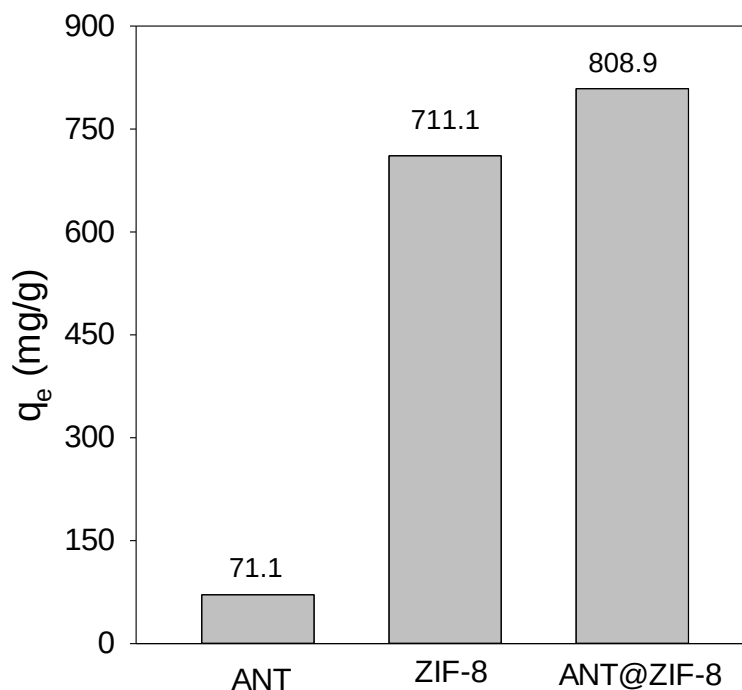


Fig. 19: Performance screening of aspirin on the ANTs, ZIF-8, and ANTs@ZIF-8. All experiments were done with the following conditions: temperature = 25 °C, pH = 6.4, an initial aspirin concentration of 100 mg/L, time = 45 minutes, and dose = 50 mg/L.

5.4 pH Effect

The impact of the pH parameter on the adsorption of aspirin pharmaceutical pollutant onto the novel nanocomposite adsorbent (ANTs@ZIF-8) was examined, and the outcomes are presented in Fig. 20. As shown in the figure, by raising the pH of the aspirin solution from 4 to 6.4, the adsorption capacity observably increased from 542.2 to 808.9 mg/g. Contrarily, beyond pH 6.4, a steep decline in aspirin adsorption was noted, reaching 216 mg/g at a pH of 12. The achievements suggest that optimal adsorption of aspirin onto the ANTs@ZIF-8 composite is achieved at pH 6.4, which is similar to findings from other researchers studying aspirin adsorption onto ZIF adsorbents [85]. For instance, in the study by Ni et al., the best adsorption capacity of aspirin on ATP@ZIF-8-DETA in the pH range of 2–10 was 320 mg/g at pH 6 [85]. Furthermore, the upward-downward trends illustrated in Fig. 20 have been reported in many adsorption studies [101,105,170–172].

ZIFs often exhibit a high pH_{PZC} and typically have a positive net surface charge at acidic and neutral pH levels. Even if ZIFs were functionalized with earth metals, they still offer a relatively high positive charge (pH range of < 8) [67]. Since the low PK_a value of aspirin ($PK_a = 3.5$) [85], the appropriate adsorption mechanism of aspirin onto ANTs@ZIF-8 is an electrostatic interaction [67]. Accordingly, within the window between 4 and 6.4 pH, aspirin and the adsorbent will possess opposite charges, which boost their electrostatic interaction. Over pH 6.4, electrostatic repulsion is anticipated, which explains the decrease in capacity at high pH. Additionally, various studies demonstrate a similar adsorption mechanism regarding the adsorption of pollutants onto different adsorbents [67,173–175].

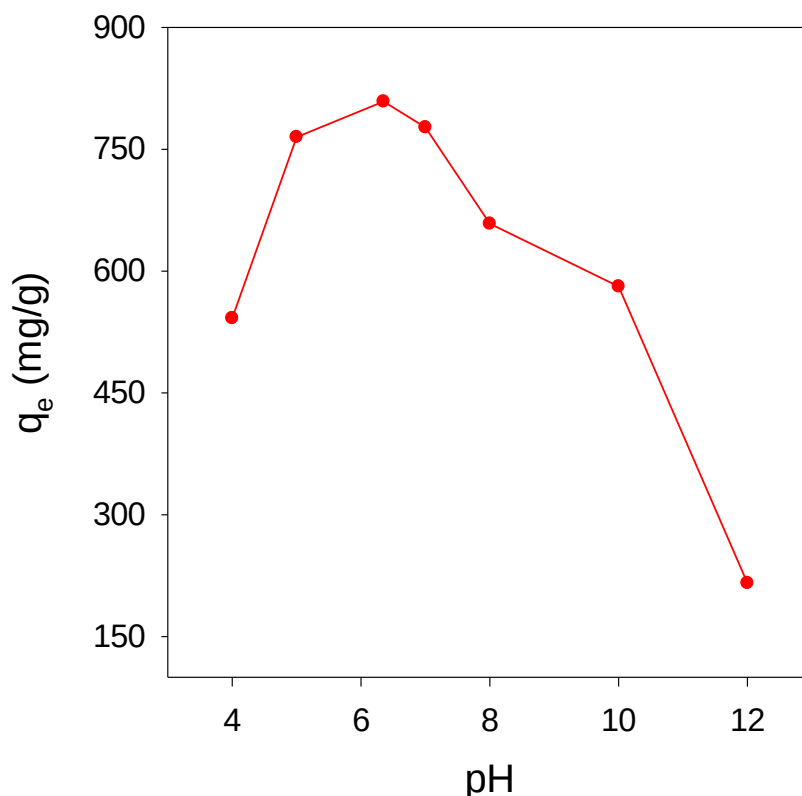


Fig. 20: pH effects on aspirin adsorption onto the ANTs@ZIF-8 composite. All experiments were done with the following conditions: temperature = 25 °C, an initial aspirin concentration of 100 mg/L, time = 45 minutes, and dose = 50 mg/L.

5.5 Adsorption isotherms

For practical applications, it is vital to determine the maximum equilibrium capacity, and the study of the adsorption isotherm offers useful details in this regard. As shown in Fig. 21, we employed a variety of different adsorption isotherm models in this study to evaluate the extent to which they fit the experimental data. The nonlinear expressions of these employed models (Langmuir, Freundlich, and Redlich Peterson) are listed in Table 8. The two-parameter Langmuir adsorption isotherm model assumes monolayer homogeneous adsorption with a finite number of identical, equivalent sites and no lateral interaction

between adsorbed molecules, while the Freundlich isotherm model represents multilayer heterogeneous surface adsorption [103]. On the other hand, the Redlich-Peterson isotherm is a combination of both Langmuir and Freundlich isotherms, using three parameters in an empirical equation [101,103].

As displayed in Fig. 21 and Table 19, the results and extracted parameters demonstrate that the Redlich-Peterson and Langmuir models are appropriate for establishing the aspirin adsorption data, as illustrated by the high R^2 values around one (0.9824 and 0.9932, respectively). Moreover, when employing the Redlich-Peterson model, an important factor to take into consideration is the dimensionless parameter (g). This g constant provides a distinction between the Freundlich and Langmuir adsorption tendencies by estimating the extent to which the adsorption action fits to either model (g close to one suitable for Langmuir or g divers from 1 tends to Freundlich). In this research, the estimated ' g ' value for aspirin is 1.2027, close to 1, suggesting that the Redlich-Peterson isotherm model closely matches the Langmuir model for aspirin adsorption [101]. The maximum removal capacity of the aspirin medicine contaminant by the ANTs@ZIF-8 adsorbent, as estimated using the Langmuir model, was 1162.9 mg/g. Likewise, in the study performed by Ni et al. [85], the maximum capacities (q_{max}) of aspirin and ibuprofen medical pollutants by the Langmuir model were 350.88 and 218.34 mg/g, respectively, with R^2 values of 0.9953 and 0.9984. Finally, the Freundlich isotherm model fails to represent the adsorption experimental data of aspirin on the ANTs@ZIF-8 composite with a R^2 value of 0.8805.

Table 19: Isotherm parameters of the Langmuir, Freundlich, and Redlich-Peterson models.

Isotherm Model	Parameters	
Langmuir	q_{max} (mg/g)	1162.9
	K_L (L/mg)	0.0279
	R^2	0.9824
Freundlich	n	3.09
	K_F ((mg/g)(L/g) ⁿ):	167.9
	R^2	0.8805
Redlich-Peterson	K_R (L/g)	23.415
	a_R (L/mg)	0.0061
	g	1.2027
	R^2	0.9932

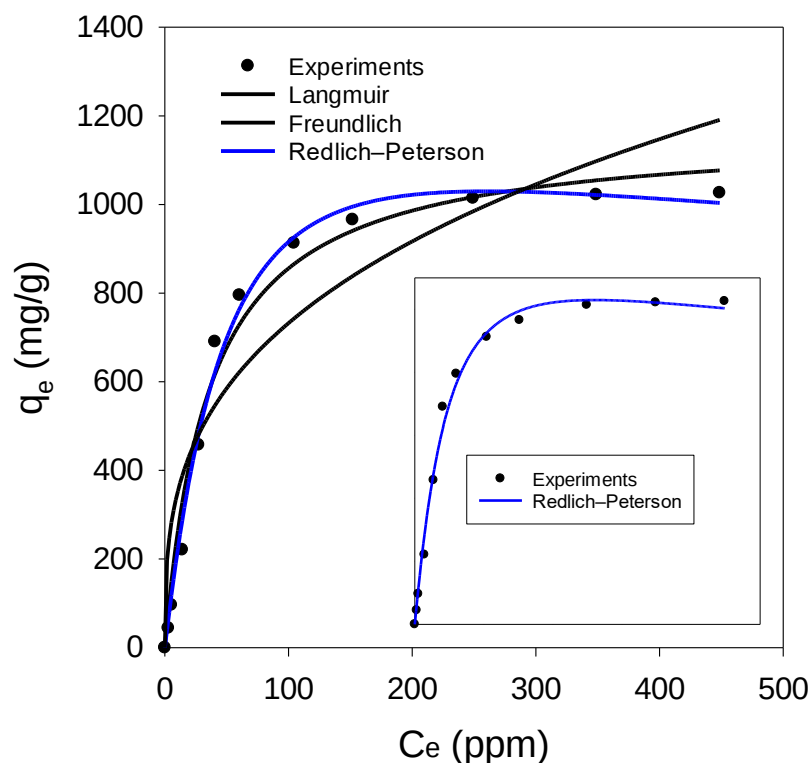


Fig. 21: Adsorption isotherm of aspirin onto the ANTs@ZIF-8 nanocomposite. All experiments were done with the following conditions: temperature = 25 °C, pH = 6.4, time = 45 minutes, and dose = 50 mg/L.

5.6 Adsorption kinetics

Adsorption is the process of transferring contaminants from the liquid to the solid adsorption medium [176]. Adsorption is a widely used method for wastewater treatment due to its simplicity, cost effectiveness, simple maintenance, and remarkable performance [177,178]. For evaluating the efficiency of novel adsorbents in wastewater treatment, it is crucial to have an extensive understanding of adsorption kinetics. The investigation of adsorption kinetics gives valuable insights into the rate of adsorption and provides vital information for the development of the adsorption system. Accordingly, the impact of contact time between adsorbent (ANTs@ZIF-8) and adsorbate (aspirin pollutant) was

measured at different time intervals, and the result is presented in Fig 22. At the first moments, the adsorption rate was significantly high, as there were many unoccupied sites on the surface of the adsorbent [102]. This high adsorption rate is indicated by a slope in the kinetic curve. Moreover, as a system approached equilibrium, the rate of the reaction decelerated. In this study, the adsorption system of aspirin onto ANTs@ZIF-8 reached equilibrium after 45 minutes. This equilibrium time is very responsible compared with many studies in literature. For instance, Ni et al. [85] found the equilibrium time of adsorption of aspirin and ibuprofen to be 40 and 50 minutes, respectively. To analyze quantitative data, the adsorption kinetics of aspirin on ANTs@ZIF-8 were regressed employing the pseudo-first-order (PFO), pseudo-second-order (PSO), and Avrami models. The suitability of these kinetic models was evaluated by comparing their estimation with the experimental results, as illustrated in Fig. 22. The obtained parameters are presented in Table 20.

As clearly demonstrated in Fig. 22 and Table 20, all three models employed in this work (PFO, PSO, and Avrami) provide a reasonably satisfactory fit of the experiment data with their respective R^2 values of 0.9914, 0.9985, and 0.9987. The PSO rate constant K_2 is 11×10^{-4} which is relatively high compared with values in literature. Based on the literature, there is a direct correlation between K_2 values and the pore size of composites [179]. Higher values of K_2 meaning higher average pore size with more available adsorption sites which explain the superior performance of ANTs@ZIF-8 compared with its bases (ANTs and ZIF-8) in screening tests. On the other side, the PFO, PSO, and Avrami kinetic models estimated aspirin's equilibrium capacity (q_e) on the ANTs@ZIF-8 adsorbent to be 793.3, 835.4, and 810.8 mg/g, respectively, while the experimental value

was 808.9 mg/g. Among these three models, the excellent and accurate model to represent the aspirin adsorption experiment data on ANTs@ZIF-8 is Avrami model with R^2 almost unity and less than 0.15 % deviation between the experimental and predicted values of equilibrium adsorption capacity.

Table 20: Predicted kinetic parameters of aspirin adsorption onto ANTs@ZIF-8.

Isotherm Model	Parameters	
Pseudo-First Order (PFO)	q_e (mg/g)	793.3
	K_1 (1/min)	0.5095
	R^2	0.9914
Pseudo-Second Order (PSO)	q_e (mg/g)	835.4
	K_2 (g/mg.min)	0.0011
	R^2	0.9985
Avrami	q_e (mg/g)	810.8
	K_a	0.2366
	$n(\frac{1}{min^n})$	0.5971
	R^2	0.9987

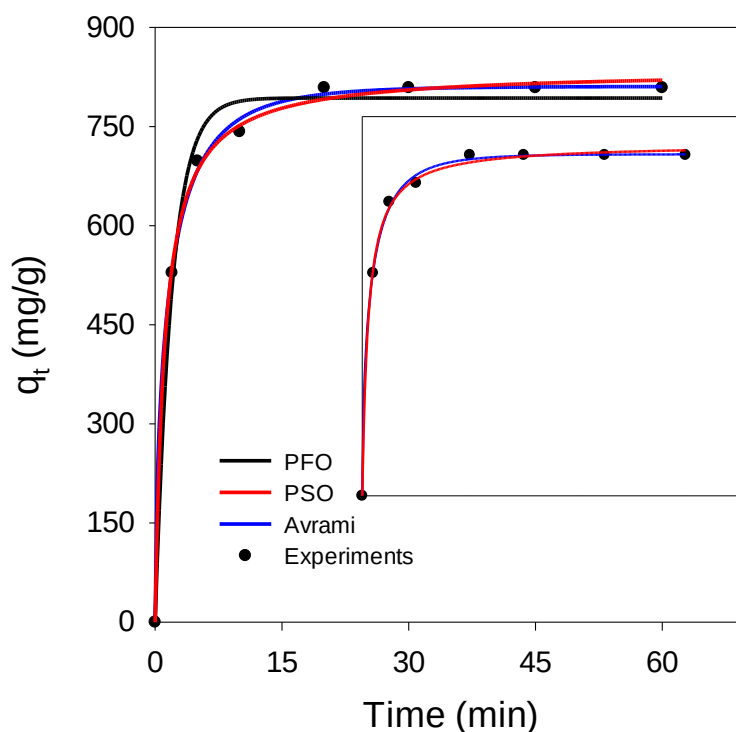


Fig. 22: Adsorption kinetics of aspirin onto the ANTs@ZIF-8 nanocomposite. All experiments were done with the following conditions: temperature = 25 °C, pH = 6.4, an initial aspirin concentration of 100 mg/L, and dose = 50 mg/L.

5.7 Thermodynamic study

The temperature has an impact on the rates at which a solute diffuses over the external layer of boundaries and through the inside pores of the adsorbents [6,109]. So, studying the thermodynamic aspects of an adsorption system offers extensive knowledge regarding the fundamentals of the adsorption process and vital thermodynamic properties such as enthalpy change (ΔH), Gibbs free energy change (ΔG), and entropy change (ΔS). Therefore, in this study, a thermodynamic analysis of the removal of aspirin by ANTs@ZIF-8 was conducted. Initially, the temperature of the aspirin-aqueous solution was changed from 25 to 55 °C. The concentrations of residual pollutants (C_e) and the

adsorption capacity at equilibrium (q_e) were measured at different temperatures (25, 40, and 55 °C). These values were utilized to compute the equilibrium constant (K_d) employing the equation (1) [180].

All thermodynamic predicted values (ΔS , ΔH , and ΔG) are negative, as summarized and presented in Table 21. The negative value of the entropy change (ΔS) of the adsorption of aspirin onto ANT@ZIF-8 indicates a reduction in the disorderliness of the systems throughout the entire process of adsorption, while the negative value of the enthalpy change (ΔH) means that it is an exothermic adsorption process. Furthermore, the negative value of Gibbs free energy change (ΔG) reveals a spontaneous adsorption process within a range between 0 and $-20 \frac{KJ}{mol}$ which means the process tends to be physisorption [151,181]. Moreover, with an increase in temperature, the change in (ΔG) becomes more negative, suggesting that the adsorption of aspirin onto ANT@ZIF-8 is more favorable at higher temperatures within the specified experimental conditions.

Table 21: Thermodynamic parameters for aspirin adsorption on the ANT@ZIF-8 composite.

T (°C)	T (K)	$q_e(\frac{mg}{g})$	$\Delta G (\frac{KJ}{mol})$	$\Delta H (\frac{KJ}{mol})$	$\Delta S (\frac{J}{mol.K})$
25	298	808.9	-6.45	-15.08	-28.94
40	313	665.2	-6.02		
55	328	560.8	-5.58		

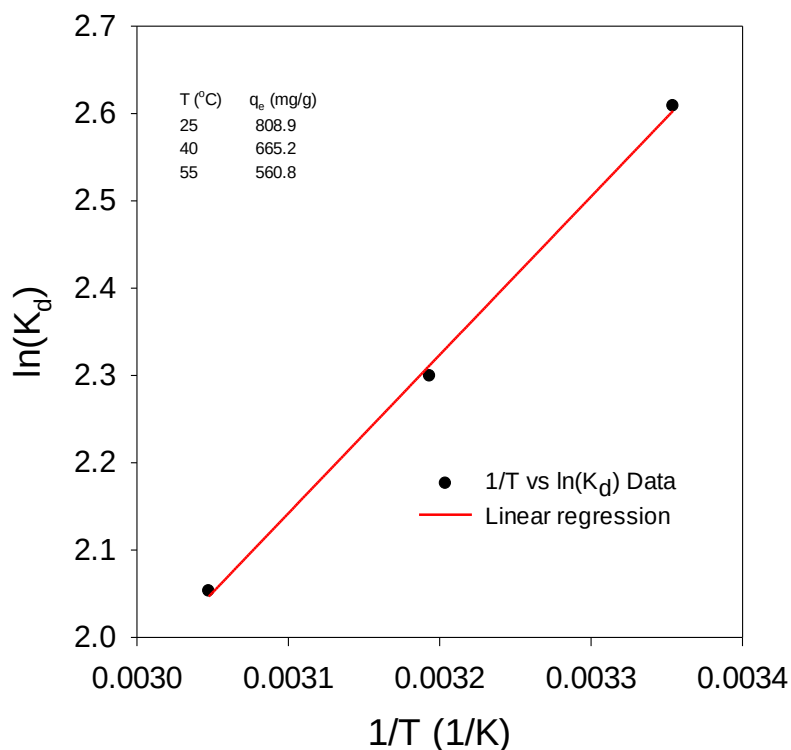


Fig. 23: A plot of the Van't Hoff equation in the range of 25-55 °C. All experiments were done with the following conditions: pH = 6.4, an initial aspirin concentration of 100 mg/L, time = 45 minutes, and dose = 50 mg/L.

5.8 Reusability of the ANTs@ZIF-8 nanocomposite

Adsorbent reusability is a vital necessity for commercial wastewater treatment applications. We examined the regeneration of the ANTs@ZIF-8 composite adsorbent after removing the aspirin pollutant for five subsequent runs using a methanol solution as an eluent. After desorbing the aspirin adsorbates with this eluent, the adsorbent was washed several times with distilled water to eliminate methanol and then dried at 65 °C in an oven. In this study, all the reusability adsorption experiments were conducted under suitable conditions: 2 g/L dosages of ANTs@ZIF-8, temperature = 25 °C, pH = 6.4, aspirin initial

concentration = 5 ppm, and contact time = 24 h. All the collected results are illustrated in Fig. 24.

As displayed in Fig. 24, the adsorption capacity of aspirin using fresh and secondarily prepared ANT@ZIF-8 adsorbents are 107.9 mg/g and 106.6 mg/g, respectively. Remarkably, the decline of adsorption capacity in the third, fourth, and fifth cycles was well accepted. 95.6 g/mg adsorption capacity for ANT@ZIF-8 in the fifth cycle compared with 107.9 mg/g for fresh adsorbent. Hence, only 11.4% of the overall performance of ANT@ZIF-8 dropped after these five cycles of removing aspirin. These results indicate the reliable stability and possibility of reuse of this adsorbent, enabling it to be an appropriate choice for purification applications.

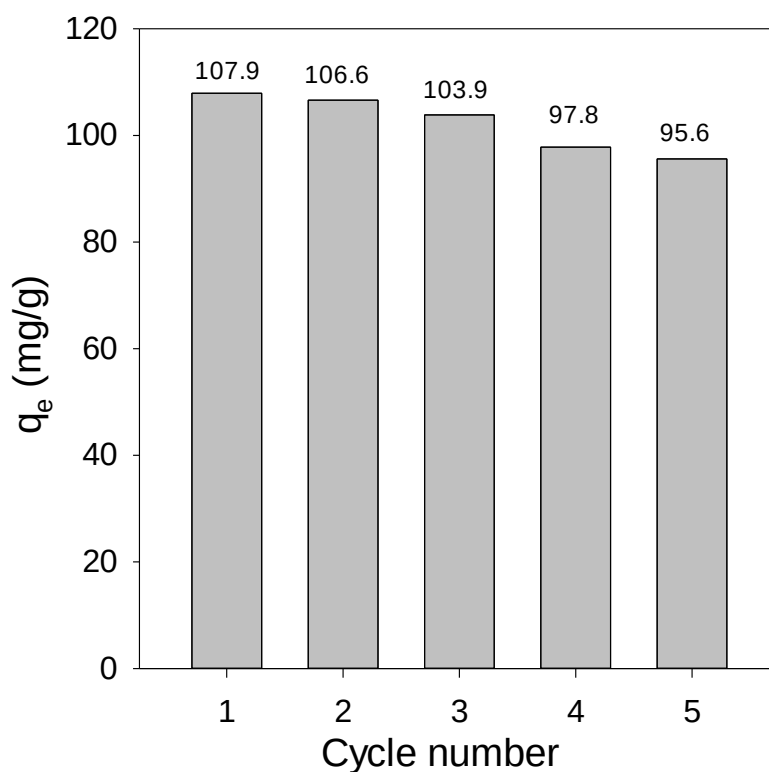


Fig. 24: Reusability of the ANT@ZIF-8 nanocomposite for the adsorptive removal of aspirin from contaminated water samples.

CHAPTER 5

ADSORPTIVE CAPABILITY OF ANT_s@ZIF-67 NANOCOMPOSITE FOR THE REMOVAL OF CRYSTAL VIOLET FROM SYNTHETIC WATER

6.1 Background

In this chapter, a metal-based ZIF novel nanocomposite was synthesized from aluminum nanotubes (ANTs) and a zinc/cobalt zeolitic imidazolate framework (ZIF-8 or ZIF-67). The surface properties, morphology, and structure of all prepared adsorbents were characterized by FTIR, N_2 adsorption, and XRD analysis. Adsorption experiments revealed the superior performance of ANT_s@ZIF-67 to remove crystal violet (CV) compared to individual components, highlighting its potential for industrial applications. The removal ratio of CV (100 ppm) by ANT_s@ZIF-67 reached up to 87%, and the CV adsorption equilibrium was achieved within 96 hours at a pH of 7, a dose of 50 mg/L, and 25 °C. The present investigation examined the impact of contact time, initial CV concentration, pH, and temperature on the adsorptive elimination of the azo dye adsorption by ANT_s@ZIF-67. The Avrami and Redlich-Peterson models exhibited the best fit of adsorption kinetic and isotherm data, with R^2 values of 0.9973 and 0.9702, respectively. Moreover, thermodynamic outcomes indicated the endothermicity and spontaneity of dye adsorption.

Another interesting result reported herein is the high stability and reproducibility of this nanocomposite, as illustrated by the minor reduction in CV removal after multiple adsorption cycles. Overall, the results demonstrate the promising capabilities of aluminum-based zeolitic imidazolate frameworks for environmental remediation purposes.

6.2 Characterization

6.2.1 X-Ray Diffraction (XRD) analysis

Fig. 25 illustrates the diffraction pattern of synthesized ANTs, ZIF-8, ZIF-67, ANTs@ZIF-8, and ANTs@ZIF-67. As can be seen, the XRD analysis of the ANTs sample displays three major diffraction peaks centered at 37.88° , 46.09° , and 67.22° , corresponding to the reflections of the (311), (400), and (440) planes, respectively. These peaks are associated with aluminum oxides and are in line with the findings reported previously [182,183]. In the case of the ZIF-8 and ZIF-67, strong and sharp 2θ peaks are almost identical and clearly observed at 7.3° , 10.4° , 12.7° , 14.7° , 16.4° , and 18° indexed to (110), (200), (211), (220), (310), and (222) crystal faces, respectively. These outcomes align with previous reports, confirming the successful formation of ZIF-8 and ZIF-67 crystals with high crystallinity [131,161,184]. Furthermore, the XRD patterns proved that the secondary composites ANTs@ZIF-8 and ANTs@ZIF-67 have preserved the original crystal structure of their parent ZIF except for a small shift in the 2θ angle. This slight shift suggests a minor expansion of the ZIF crystallinity and could be explained by a deformation produced by repulsive interactions between the ANTs and imidazole groups. Contrarily, the XRD peaks

associated with ANTs observably disappeared in the composites, which is attributed to poor interaction with ZIF particles.

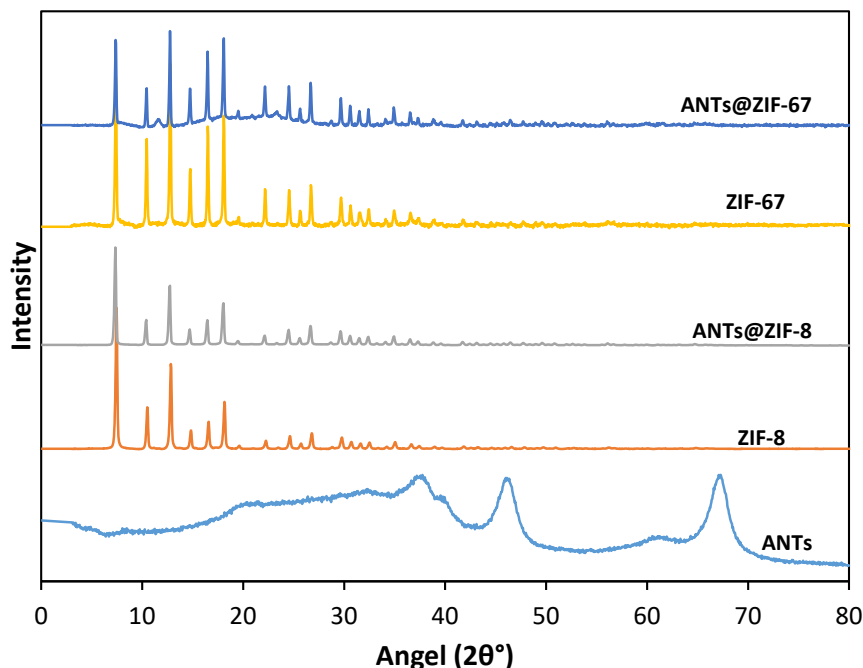


Fig. 25: XRD patterns of the adsorbents: ANTs, ZIF-8, ZIF-67, ANTs@ZIF-8 and ANTs@ZIF-67.

6.2.2 Fourier Transform Infrared (FTIR) spectroscopy analysis.

The FTIR analysis ($4000\text{--}400\text{ cm}^{-1}$) for ANTs, ZIF-8, ZIF-67, and their combination was conducted during the adsorption process, and the outcomes are illustrated in Fig. 26. As can be observed, the FTIR spectra of the ANTs sample display a major peak at 510 cm^{-1} , corresponding to the Al-O bonds [120,126,162]. Moreover, three minor bands can be observed at 3397 , 1635 , and 1097 cm^{-1} , indicating the OH, H-O-H, and Al-O-H vibration bonds, respectively [120,162].

According to Fig. 26, the ZIF-8 adsorbent has all the same peaks of 2-methyl imidazole, with only one extra peak seen around 420 cm^{-1} , which corresponded the Zn-N bond, matching those previously reported [160,163,185]. The ZIF-8 band at 1145 cm^{-1} associated with the aromatic C–N bending mode, while the peak at 1581 cm^{-1} arose from the C=N stretch vibration [159,163]. Moreover, there were some other sharp bands in the range of $900\text{--}1400\text{ cm}^{-1}$ and below 800 cm^{-1} , that might be attributed to the in-plane bending and out-of-plane bending of the ring, respectively [122,123]. In the case of the ZIF-67 sample, the absorption band at 424 cm^{-1} is related to the presence of the Co-N bond, while the other sharp peaks are similar to those of ZIF-8 [122,186]. Interestingly, the FTIR spectra of the secondary composites (ANTs@ZIF-8 and ANTs@ZIF-67) are almost compatible with ZIF-8 and ZIF-67, involving and including Zn-N, Co-N, C-N, and C=N signals, confirming the presence of ZIF-8 and ZIF-67 in both secondary composites. Conversely, the AL-O peak from ANTs was clearly reduced in both composites, indicating that there was a weak interaction between the ZIF and aluminum particles.

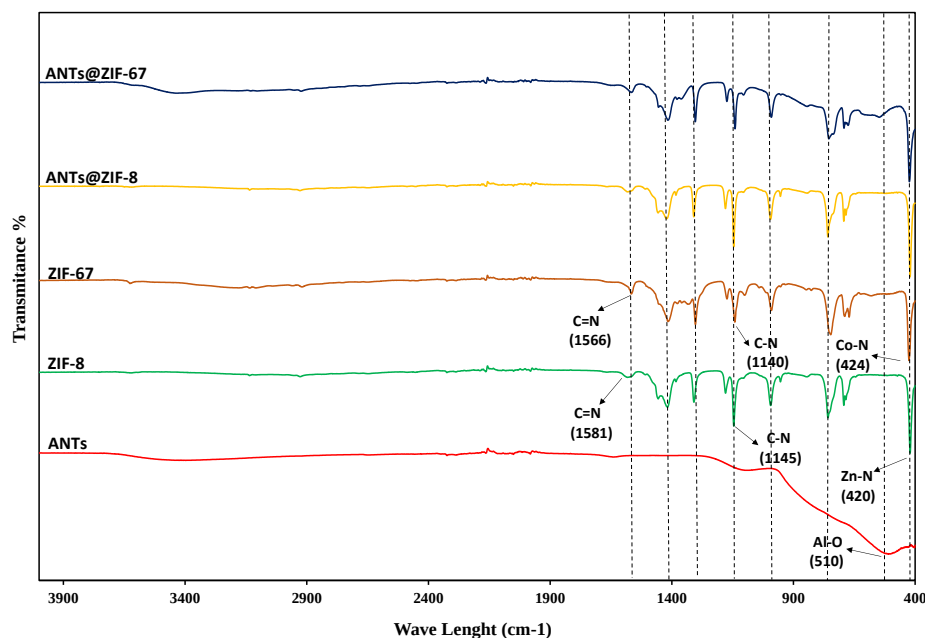


Fig. 26: FTIR spectra of ANTs, ZIF-8, ZIF-67, ANTs@ZIF-8 and ANTs@ZIF-67.

6.2.3 Brunauer-Emmett Teller (BET) analysis

The porosity measurements and (S_{BET}) have been examined, and the outcomes of the N_2 adsorption-desorption plots are displayed in Fig. 27. According to the IUPAC classification, the nitrogen isotherm of the aluminum nanotubes (ANTs) sample belongs to isotherms of IV type, indicating the existence of micropores and the gradual increase of N_2 uptake with increasing a relative pressure value. At relative pressure (P/P_0) beyond 40%, the N_2 isotherms demonstrated significant hysteresis, suggesting an absence of mesopores on the surface of the ANTs adsorbent, in addition to the existence of reversible capillary condensation in the sample mesopores. The findings are in line with those reported previously [125,127,182].

As displayed in Fig. 27, the ZIF-8 and ZIF-67 demonstrate comparable hysteresis loops, indicating similar levels of porosity for both samples. The standard type I isotherms of both ZIFs suggest that adsorption takes place in the micropore structure due to strong interactions between the adsorbent and adsorbate. Comparable findings have been reported in previous research [130,131,184,187]. Furthermore, the secondary composites ANTs@ZIF-8 and ANTs@ZIF-67 conserved this microporous texture of the original ZIF, as evidenced by a type I isotherm for both samples. However, the N_2 uptake was reduced due to the partial inclusion of the ANTs units within the cavities of ZIFs.

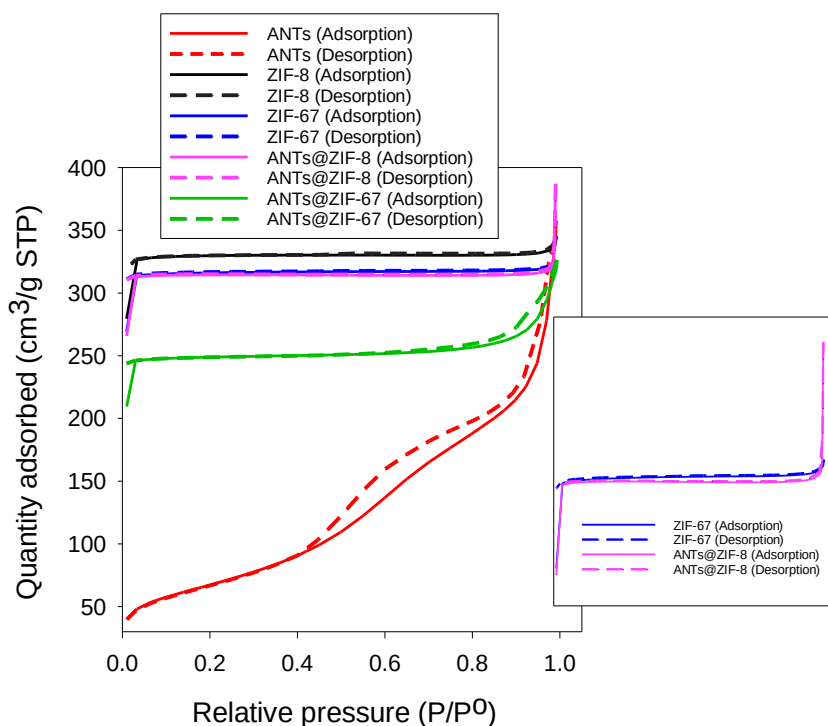


Fig. 27: Isotherms of N_2 adsorption on and desorption from ANTs, ZIF-8, ZIF-67, ANTs@ZIF-8, and ANTs@ZIF-67 nanocomposites. The inset shows the isotherms of N_2 adsorption on and desorption from ZIF-67 and ANTs@ZIF-8 nanocomposite.

The corresponding textural features of all prepared adsorbents, including the S_{BET} Langmuir specific surface area, V_p , and d_p were summarized in Table 22. The ZIF-8

sample has illustrated a high BET surface area of $1209 \text{ m}^2/\text{g}$ and a total pore volume of $0.028 \text{ cm}^3/\text{g}$, while the ANTs and ZIF-67 samples demonstrated a S_{BET} of 237.5 and $1158.2 \text{ m}^2/\text{g}$, respectively. As expected, the ANTs@ZIF-8 sample exhibited a lower BET surface area compared to that of the bare ZIF-8 sample (approximately 4.4%), while the ANTs@ZIF-67 composite demonstrated a S_{BET} of $912.8 \text{ m}^2/\text{g}$, which represents only 78.8% of the BET surface area of ZIF-67. The outcomes obtained from this research were compared with the previously reported findings, as shown in Table 22.

Table 22: Textural properties of ANTs, ZIF-8, ZIF-67, ANTs@ZIF-8, and ANTs@ZIF-67 nanocomposites.

Adsorbent	S_{BET} (m^2/g)	Langmuir Specific Surface Area (m^2/g)	V_p (cm^3/g)	d_p (nm)	Ref.
ANTs	237.5	348.3	0.565	7.25	This study
ZIF-8	1209.0	1442.0	0.028	1.71	This study
ZIF-67	1158.2	1382.1	0.020	1.71	This study
ANTs@ZIF-8	1155.4	1373.6	0.114	1.7	This study
ANTs@ZIF-67	912.8	1090.1	0.130	2.00	This study
Commercial γ - Al_2O_3	215	-	1.23	11.9	[127]
ZIF-8	889.7	-	0.036	11.64	[188]
ZIF-8	1228	1896	0.5850	-	[160]
ZIF-67	1094.3	-	-	2.106	[189]
ZIF-67	1995	-	0.74	1.5	[131]

6.2.4 Scanning Electron Microscopy and Energy Dispersive Spectrometry (SEM/EDS) analysis

The morphologies of ANTs, ZIF-8, ZIF-76, and their combination were investigated by scanning electron microscopy (SEM), and the results are presented in Fig. 28a–e. The SEM image of the ANTs sample demonstrates the agglomerated nanotube shape of aluminum oxides, as shown in Fig. 28a. Moreover, the EDX analysis reveals that the sample comprises AL and O elements, confirming ANT formation [132,164]. Remarkably, the high-resolution images (Fig. 28b, c) illustrate the homogeneous rhombic dodecahedral structures of ZIF-8 and ZIF-67, in line with the literature [133–135,166,167]. The morphologies of ANTs@ZIF-8 and ANTs@ZIF-76 composites clearly show that the surface of ZIFs has been decorated with aluminum nanotubes, as illustrated in Fig 3e, f. The EDX analysis also supports this manner of uniform distribution of elemental composition compared to the corresponding ZIF. The elemental compositional analysis for all samples is presented in Table 23. For instance, the ANTs@ZIF-67 contained cobalt of 22 wt.% compared to 22.3% for ZIF-67, while the ANTs@ZIF-8 exhibited 16.0 wt.% zinc compared to 20.5% for ZIF-8. This composition ensures the well-functioning of the ANTs without having a large impact on ZIF's structure.

Table 23: Elemental analysis of ANTs, ZIF-8, ZIF-67, ANTs@ZIF-8 and ANTs@ZIF-67.

Element wt.% / Adsorbent	ANTs (This study)	ANTs@ZIF-8 (This study)	ANTs@ZIF-67 (This study)	ZIF-8 [157]	ZIF-67 [135]
C	-	44.2	38.5	57.9	44.1
N	-	30.8	22.9	26.1	34.4

Zn	-	20.5	-	16.0	-
Co	-	-	22	-	22.3
AL	38.1	0.7	2.9	-	-
O	69.9	3.8	13.8	-	3.3

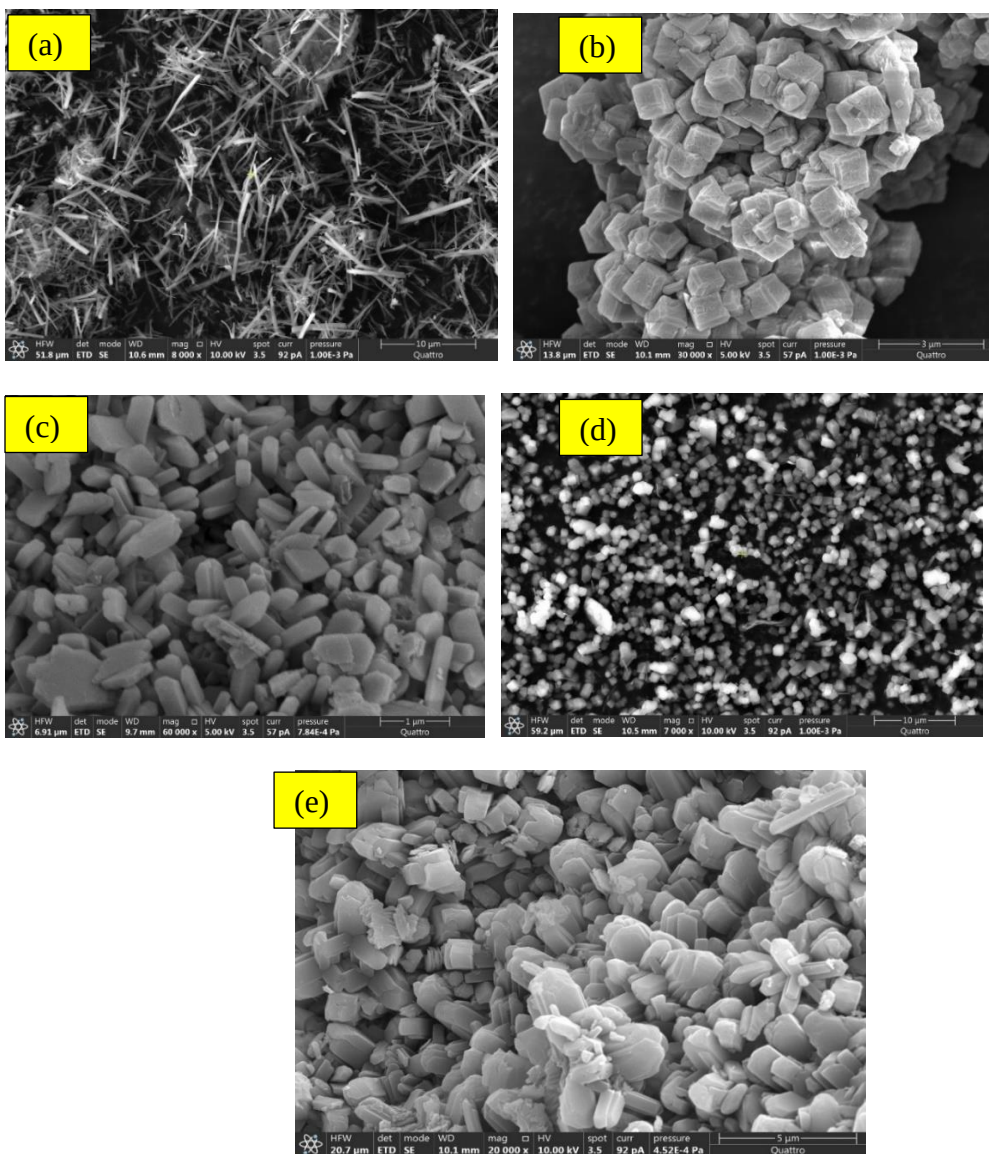


Fig. 28: SEM images of (a) ANTs, (b) ZIF-8, (c) ZIF-67, (d) ANTs@ZIF-8, and (e) ANTs@ZIF-67.

6.3 Adsorbent screening

The global water pollution issue has significantly increased in recent decades, which necessitates the development of more potential adsorbents for wastewater remediation. In this study, aluminum nanotubes (ANTs) were prepared, and their ability to remove crystal violet contaminants was examined. As demonstrated in Fig. 29, the adsorption capacity of CV (125.6 mg/g) using ANTs is notably low. However, ZIFs have been considered effective materials for their efficient elimination from water bodies. For example, Usman Ismail et al. [109] examined the adsorption of CV using ZIF-60, achieving an adsorption capacity of 471.71 mg/g. In addition to that, Liu et al. [190] investigated the ability of ZIF-67 to remove CV, reaching capacity of 606 mg/g.

In recent studies, functionalizing metals, or other suitable materials for ZIFs to make metal-based ZIF adsorbents has become a more common way to improve adsorption performance. According to Tyagi et al. [191], the efficacy of WS_2 /ZIF-9 achieved a capacity of 2124 mg/g in the removal of CV pollutants. Among all of these, the adsorption capacity of crystal violet on DSAC@ZIF-8 is 638.99 mg/g, according to Al-Hazmi et al. [4]. In this study, ANTs, ZIF-67, ZIF-8, and their composite (ANTs@ZIF-67 and ANTs@ZIF-8) were synthesized and underwent comprehensive screening tests to evaluate their efficiency in removing CV dye, as is clearly shown in Fig. 29. All these screening tests were performed with the standard conditions: temperature = 25 °C, pH of 6.4, CR initial concentration = 100 ppm, time of 96 hours, and dose of 50 mg/L.

As displayed in Fig. 29, the adsorption capacities of CV on aluminum nanotubes, ZIF-8, and ZIF-67 base materials are 125.6, 1337.1, and 1581.4 mg/g, respectively. Contrarily, the ANTs@ZIF-67 nanocomposites achieved a higher capacity (1637.8 mg/g) compared

with both bases, while the ANTs@ZIF-8 adsorbent showed relatively low adsorption capacity. Although the difference between the composite and one of its bases is relatively low (3.4%), it still has potential and attractive behavior in wastewater treatment. Inspired by the metal base-ZIF (ANTs@ZIF-67) adsorbent for removing CV pollutants from aqueous systems, we selected it for further investigation studies in the following sections. The studies will emphasize kinetic and isotherm analyses, temperature effects, contact time, pH impacts, and the potential for reuse.

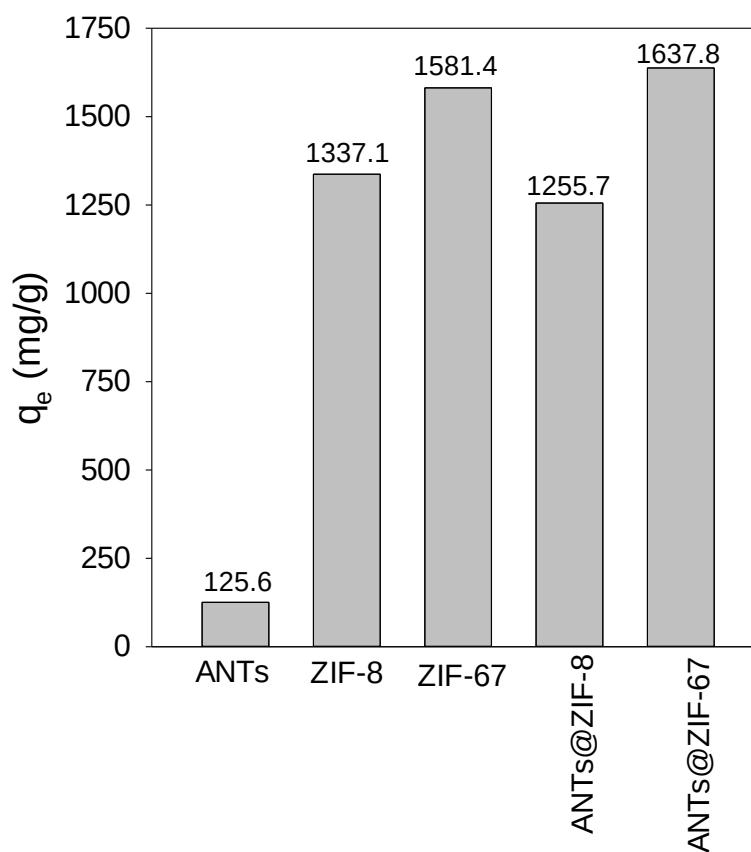


Fig. 29: Performance screening of CV dye on the ANTs, ZIF-8, ZIF-67, ANTs@ZIF-8, ANTs@ZIF-67. All screening experiments were done with the standard conditions: temperature = 25 °C, pH = 6.4, CV concentration = 100 ppm, time = 96 hours, and dose = 50 mg/L.

6.4 pH Effect

The pH of the adsorption solution impacts the ionization rates of adsorbents and adsorbates, which impacts the overall efficiency of the adsorption process. According to Ighalo et al. [67], the zeolitic imidazolate frameworks (ZIFs) usually offer a net positive surface charge. Furthermore, the combination of these ZIFs with metals still exhibits relatively high pH_{PZC} [67]. Hence, the pH of the adsorption medium of CV cationic dye onto the developed nanocomposite was independently varying from 4 to 10 while keeping other adsorption parameters constant. These experiments were conducted at room temperature with a dose of 50 mg/g, an initial concentration of 100 mg/g, and a contact time of 96 hours. Fig. 30 demonstrates this influence of pH on CV adsorption onto the ANTs@ZIF-67 composite. As shown in Fig. 30, the adsorption efficiency sharply increased in pH from 4 to 5, with capacities of 258 and 1566 mg/g, respectively. This fast growth is due to the positively charged CV molecules' ability to neutralize additional negative charges on the surface of the ZIF nanocomposite. Moreover, beyond a pH of 5, the behavior of the adsorption process followed a gradual increase, achieving 1728 mg/g at a pH of 7. This semiregular increment in adsorption performance was continued, reaching 1929 at pH 10. The higher adsorption at higher pH levels can be attributed to the electrostatic interaction between the negatively charged sites of the developed adsorbents and the positively charged CV molecules. Based on the above result, high pH levels (9–10) are the best condition for crystal violet dye adsorption using the ANTs@ZIF-67 adsorbent, which is in agreement with the findings from many adsorption studies in the literature [4,96,192].

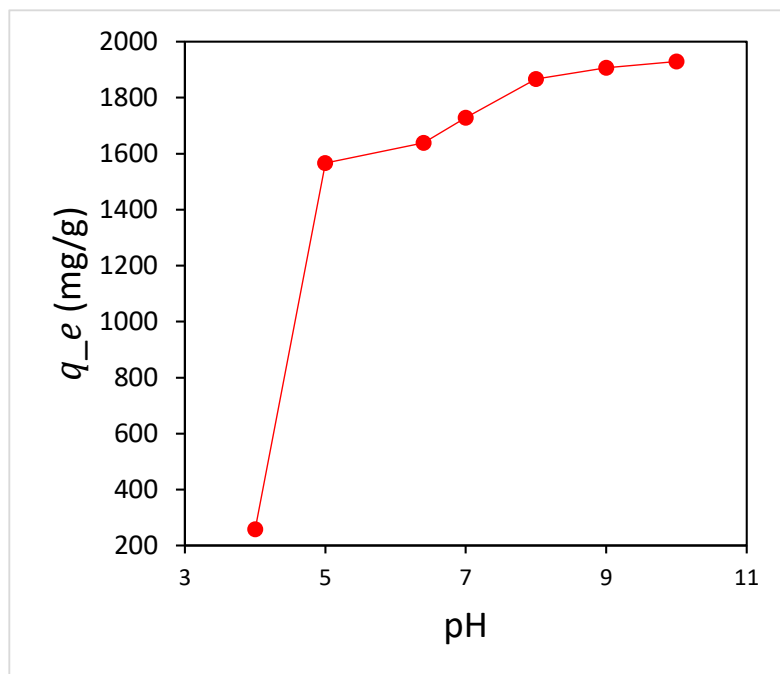


Fig. 30: pH effects on CV dye adsorption onto the ANTs@ZIF-67 nanocomposite. The adsorption was performed under the conditions: a contact time of 96 hours, 25 °C, 100 ppm of an initial CV concentration, and a dosage of 50 mg/L.

6.5 Adsorption kinetics

Adsorption kinetic investigations offer crucial details about the rate and mechanism of adsorption of a specific water contaminant onto an adsorbent surface under certain conditions [141]. Therefore, the kinetics tests were performed to collect data regarding CV adsorption onto ANTs@ZIF-67 (the best performance adsorbent in screening). The contact time between the developed adsorbent and the CV adsorbate varied until reaching equilibrium. All kinetic tests were performed under the same conditions: room temperature, a pH of 6.4, a 100-ppm initial CV concentration, a dosage of 50 mg/L, and shaking at 250 rpm. This experimental data was analyzed using the non-linear regression of the kinetics models, which include the PFO, PSO, and Avrami models. The relevant fitting curves are

displayed in Fig. 31. The obtained parameters from this analysis of the adsorption data using the mentioned kinetics models are also summarized in Table 24. As demonstrated in Fig. 31. Initially, the adsorption rate of the CV is quite high, but it gradually levels off as time goes on, meaning that equilibrium has been achieved. In this study, the adsorption system of CV onto ANTs@ZIF-67 reached equilibrium after 96 hours. This equilibrium time is very responsible compared with many studies in literature. For instance, according to Ismail et al. [109], the CV adsorption onto ZIF-60 achieved equilibrium time approximately of 75 h.

Table 24: Estimated kinetic parameters of CV adsorption onto the developed ANTs@ZIF-67.

Isotherm Model	Parameters	
PFO	$q_e(\text{mg/g})$	1634.7
	$K_1 \text{ (1/min)}$	0.0587
	R^2	0.9879
PSO	$q_e(\text{mg/g})$	1936.6
	$K_2 \text{ (g/mg.min)}$	3.42×10^{-5}
	R^2	0.9969
Avrami	$q_e(\text{mg/g})$	1786.3
	K_a	0.0295
	$n(\frac{1}{\min^n})$	0.7488
	R^2	0.9973

As clearly demonstrated in Fig. 31 and Table 24, the outcomes indicate that the PSO and Avrami models give the best fit to the kinetic data with R^2 values of 0.9969 and 0.9973, suggesting that both chemisorption and physisorption are significant factors in the adsorption process [176,193]. The higher value of PSO constant ($K_2 = 3.42 \times 10^{-5}$ g/mg.min) indicates high average pore size and more effective adsorption sites, which support the high effectiveness of composite in screening tests [179]. On the other side, the predicted equilibrium capacity (q_e) of CV by PSO and Avrami models were 1936.6 and 1786.3 mg/g, respectively, compared with 1637.8 mg/g of experimental value. Furthermore, PFO also achieves an acceptable fit to experimental data with an R^2 value of 0.9879 and a predicted equilibrium capacity of 1634.7 mg/g (only 0.2% deviation from the experimental value).

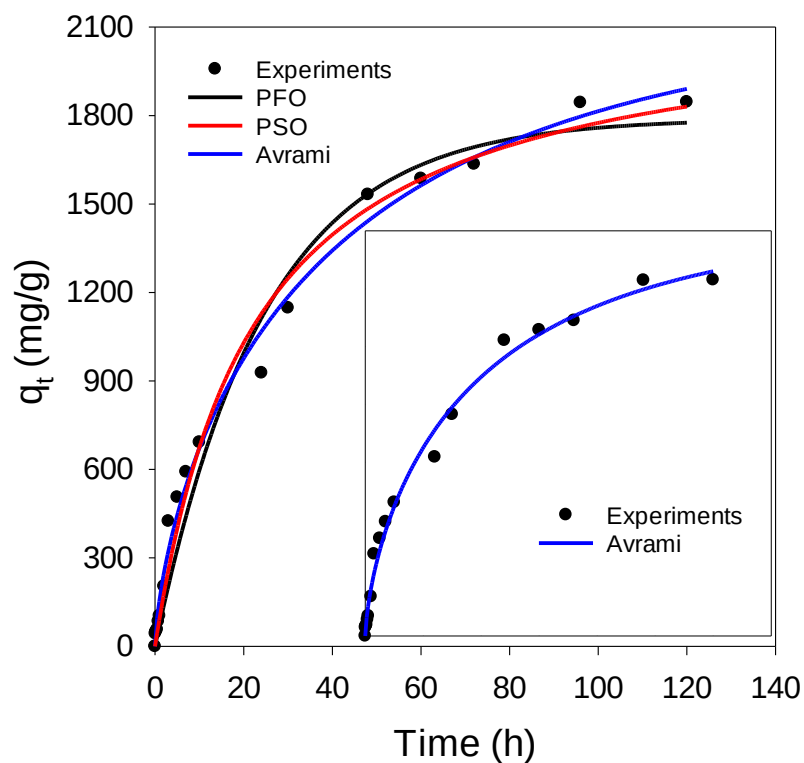


Fig. 31: Adsorption kinetics of CV dye onto ANTs@ZIF-67. All kinetic experiments were done with the standard conditions: temperature = 25 °C, pH = 6.4, CV concentration = 100 ppm, and dose = 50 mg/L.

6.6 Adsorption isotherms

The investigation of adsorption isotherms is essential to evaluating the efficiency of new adsorbents. Therefore, we conducted tests to examine the adsorption of crystal violet onto the developed composite, employing different initial CV concentrations. Then, we applied non-linear isotherm models (Langmuir, Freundlich, and Redlich-Peterson) to analyze the equilibrium adsorption capacities and remaining dye concentrations. The mathematical expressions for these isotherm models can be found in the section on materials and methods. Fig. 32 depicts the adsorption isotherm of CV onto the ANTs@ZIF-67

composite, and Table 25 lists the parameters obtained by fitting the experimental data using these isotherm models. As demonstrated in the Fig. 32, the regression curves indicate the better accuracy of both the Langmuir models and Redlich-Peterson in representing the CV adsorption data, with an R^2 values of 0.9827 and 0.9830, respectively. According to the Langmuir model, the ANTs@ZIF-67 composite had a maximum adsorption capacity for CV of 3391.8 mg/g. Additionally, the Redlich-Peterson isotherm model gives a dimensionless constant ($g = 0.9702$) that is very close to 1. This means that the Redlich-Peterson model is more like the Langmuir model (homogenous solution) than the Freundlich model (heterogenous adsorption) for CV adsorption [101]. Finally, the Freundlich model display more pronounced deviations from the CV adsorption data, indicated by an R^2 value of 0.9306.

Table 25: Predicted isotherm parameters of crystal violet adsorption onto ANTs@ZIF-67.

Isotherm Model	Value of Parameters	
Langmuir	q_{max} (mg/g)	3391.8
	K_L (L/mg)	0.0500
	R^2	0.9827
Freundlich	n	3.01
	K_F ((mg/g)(L/g) ⁿ):	512.6
	R^2	0.9306
Redlich-Peterson	K_R (L/g)	182.3
	a_R (L/mg)	0.06535
	g	0.9702
	R^2	0.9830

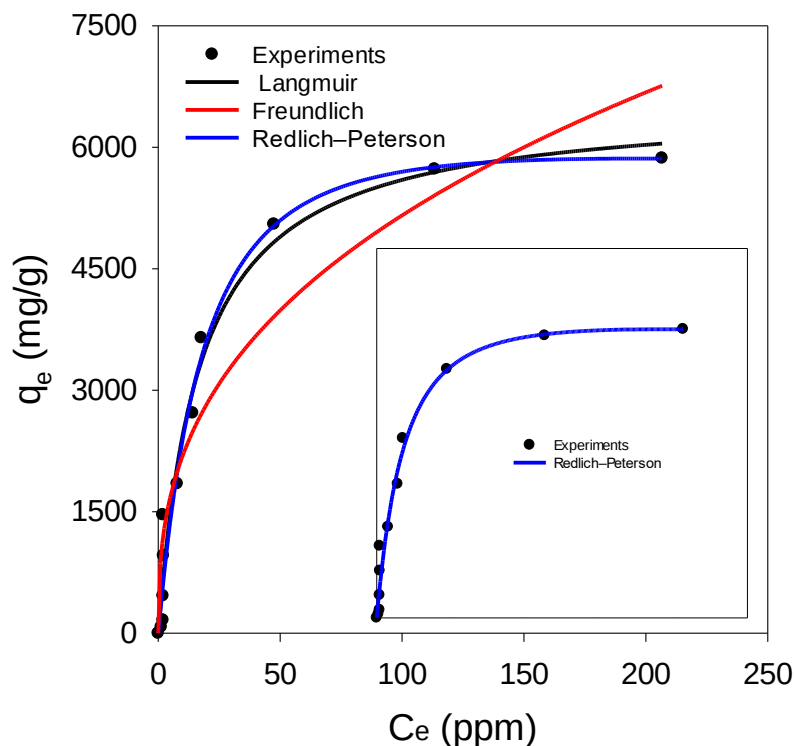


Fig. 32: Adsorption isotherm of CV dye onto ANTs@ZIF-67. All isotherm experiments were done with the standard conditions: temperature = 25 °C, pH = 6.4, time = 96 hours, and dose = 50 mg/L.

6.7 Thermodynamic study

The effect of temperature on crystal violet adsorption processes using ANTs@ZIF-67 nanocomposite was examined, and thermodynamic analysis was performed in accordance with the findings. Initially, the temperature of the CV-aqueous solution was independently varied from 10 to 55 °C, and the adsorption capacity at equilibrium (q_e) and the concentrations of residual contaminants (C_e) were measured at each temperature (10, 25, 55 °C). The equilibrium constant (K_d) was calculated using the equation (1) [101]. The

experiments were conducted for 96 hours at pH 6.4, 50 mg/L of adsorbent dose, and 100 ppm CV concentration. Fig. 33 shows the $\ln(K_d)$ -1/T graph for the processes.

These predicted thermodynamic properties (ΔS , ΔH , and ΔG) are summarized in Table 26.

The calculated ΔH of the CV adsorption system is $35.63 \frac{KJ}{mol}$, indicating that the CV adsorption onto the ANTs@ZIF-67 composite is an endothermic process (absorbs heat) [149,150]. For the positive value of ΔS ($165.4 \frac{J}{mol.K}$), suggesting increase of randomness at the interface [194]. In addition, all calculated values of ΔG are negative values across all examined temperatures, suggesting that CV adsorption onto the ANTs@ZIF-67 composite is a spontaneous process [87]. Moreover, rising in temperature of the adsorption system leads to higher adsorption, which indicates a more favorable adsorption with an increase in equilibrium capacity from 13311.8 mg/g at 10 °C to 1878.4 mg/g at 55 °C. Besides demonstrating the spontaneous nature of adsorption, ΔG values can also provide information about the type of adsorption. ΔG values ranging from -400 and -80 kJ/mol reflect chemical adsorption, while values between 0 and -20 kJ/mol reflect physical adsorption, and values between -80 and -20 kJ/mol point to a combination of physical and chemical adsorption [151,181]. In this study, all ΔG values within a range of 0 and $-20 \frac{KJ}{mol}$, that it is likely the physical nature of adsorption.

Table 26: Thermodynamic parameters of the adsorption of CV on ANT@ZIF-67.

T (°C)	T (K)	$q_e (\frac{mg}{g})$	$\Delta G (\frac{KJ}{mol})$	$\Delta H (\frac{KJ}{mol})$	$\Delta S (\frac{J}{mol.K})$
10	283	1311.8	-8.66		
25	298	1637.8	-11.01		
55	328	1878.4	-15.71	35.63	165.4

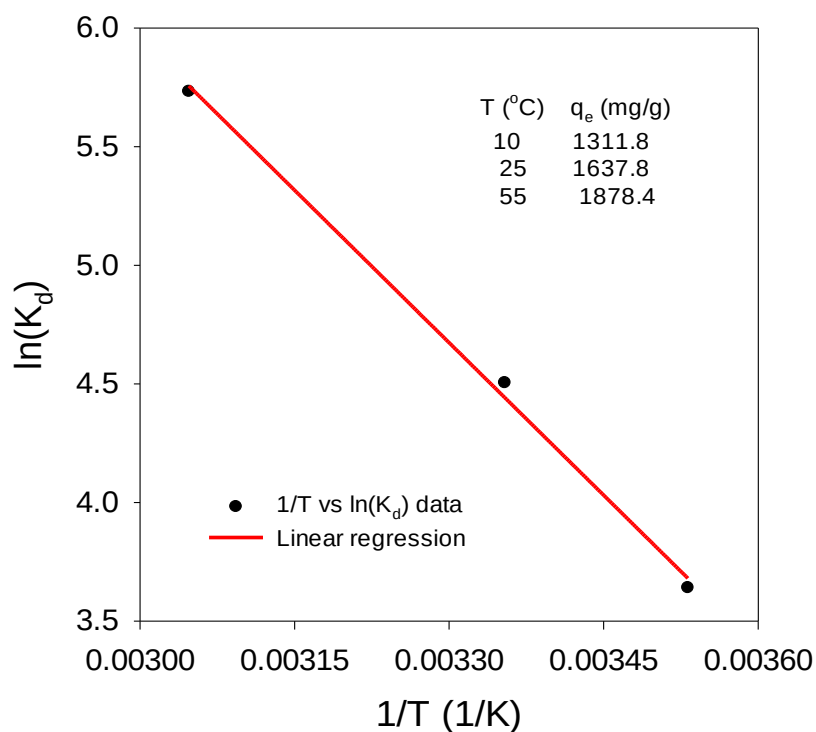


Fig. 33: Plot of the Van't Hoff equation in the range of 10-55 °C.

6.8 Reusability of the ANT@ZIF-67 nanocomposite

The practical potential of any adsorbent for applications in industry can be evaluated by examining its regeneration and reusability processes. If the adsorbent materials demonstrate outstanding efficacy throughout multiple cycles of reusing, the cost of wastewater treatment could be significantly lowered. In this study, all the reusability

adsorption experiments were conducted under optimized conditions: 2 g/L dosages of ANTs@ZIF-67, 5 mg/L (ppm) of CV solution at pH 6.4, a contact time of 24 h, and stirring at 250 rpm at room temperature. Methanol-washing was used to refresh the composite by eliminating any residual adsorbates from the adsorbents' surface. As shown in Fig. 34, the efficiency of the first adsorption cycle was 99.6%. This excellent performance is still in the second and third cycles, with reducing percentages of 1 and 3%, respectively. However, this observably dropped to approximately 91% for the fourth cycle and 85% for the fifth cycle. This reduction could be due to the decreasing adsorbent sites because of the adhesion of CV molecules to the surface of the adsorbents from previous cycles. In addition, the suggested adsorption type in this study is physical adsorption, as indicated in the thermodynamic studies section, which explains the easy regeneration of spent adsorbent.

Overall, the adsorption performance of ANTs@ZIF-67 displayed an interesting outcome with a slight reduction in the percentage of CV removal (approximately 20%). These results confirmed the potential stability and recoverability of the ANTs@ZIF-67 composite, making it a trusted option for water treatment applications.

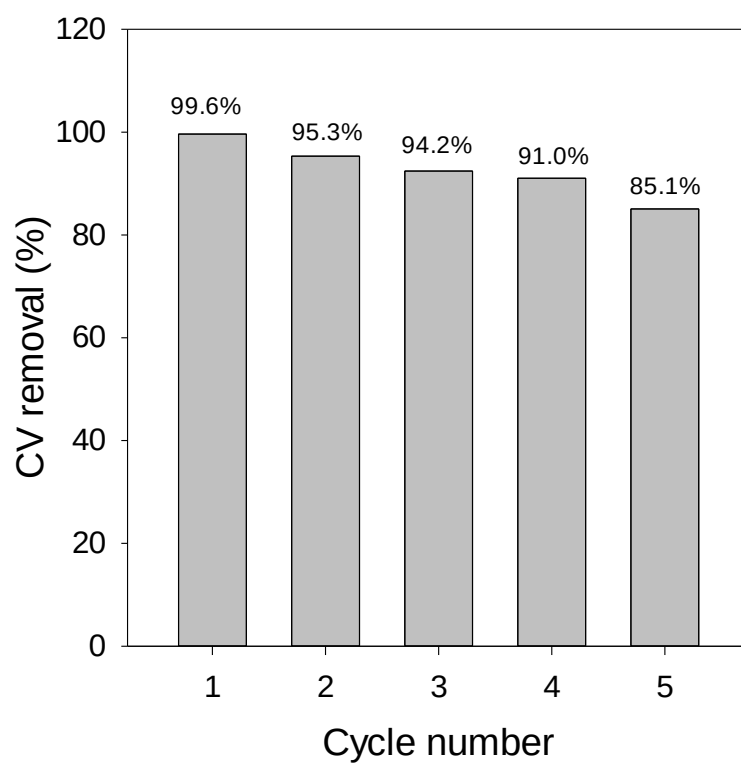


Fig. 34: Desorption and reusability of ANTs@ZIF-67 nanocomposite.

CHAPTER 7

CONCLUSION AND RECOMMENDATION

7.1 Conclusion

In conclusion, several adsorbents, including ANTs, ZIF-8, ZIF-67, ANTs@ZIF-8, and ANTs@ZIF-67, were synthesized, characterized, and used for the removal of Congo red, crystal violet, and aspirin from the aqueous solutions. The characterization techniques, including BET, XRD, and FTIR analysis, were employed to provide valuable insights into the surface morphology, porous structure, crystalline nature, and surface functional groups of all prepared adsorbents. The XRD spectrum of base materials (ANTs, ZIF-8, and ZIF-67) demonstrated the same sharp peaks as in the literature, confirming the successful synthesis of the adsorbents. In addition to that, the secondary composites (ANTs@ZIF-8 and ANTs@ZIF-67) exhibited the same spectrum of corresponding ZIF, indicating that the crystal structure was still unchanged in all composites. Furthermore, the N_2 adsorption-desorption plots of all samples except ANTs displayed the type I isotherm according to the IUPAC classification, which is typical for microporous adsorbents.

Among these, the ANTs@ZIF-67 nanocomposite achieved superior results compared with its parent materials and many other adsorbents in the literature for the removal of CR and CV with adsorption capacities of 505 and 1638 mg/g, respectively, at an experiment condition: room temperature, pH = 6.4, an initial aspirin concentration of 100 mg/L, time

= 96 hours, and dose = 50 mg/L. Moreover, a positive net surface charge of metal-based ZIF composites with a negative CR charge (anionic dye) demonstrated an electrostatic interaction as potential adsorption mechanisms, which was confirmed by the downward trend of CR adsorption within the pH range between 4 and 10. Moreover, the positive charge of CV (cationic dye) displayed an upward trend with the same composite, confirming the electrostatic interaction adsorption mechanism. Accordingly, the maximum adsorption capacity achieved for CR dye was 1090 mg/g at a pH of 4, while a higher adsorption capacity for CV was found to be 1929 mg/g at a pH of 10.

Moreover, the effects of other operative parameters, such as initial pollutant concentration, contact time, and thermodynamic studies, have been investigated. The initial CR and CV concentrations were changed in the range (5–500) independently, while all other parameters were kept constant for collecting isotherm data. The isotherm data were regressed using three isotherm models (Langmuir, Freundlich, and Redlich-Peterson). The outcomes indicated that the Redlich-Peterson model nicely represented the experimental results for both CR and CV adsorption, with R^2 values of 0.9928 and 0.9830, respectively. Likewise, the regression of kinetic data was employed using three models (PFO, PSO, and Avrami models). The Avrami model precisely predicted the kinetic data for CR and CV removal with R^2 values of 0.9930 and 0.9973, respectively. The thermodynamic analysis illustrated the endothermicity and spontaneous nature of CR and CV adsorption with positive values of ΔH and ΔG properties.

In this study, we also investigated the uptake of aspirin as a pharmaceutical pollutant from aqueous solutions utilizing ANTs@ZIF-8. We have conducted screening experiments that demonstrate this composite's potential for pharmaceutical removal when compared to

parental materials and multiple adsorbents in the literature. The ANTs@ZIF-8 nanocomposite exhibited a maximum aspirin adsorption capacity of 808 mg/g at 25 °C and a pH of 6.4. The kinetic and isotherm data of aspirin adsorption were collected and regressed using various models. We employed three kinetic models (PFO, PSO, and Avrami) and three isotherm models (Langmuir, Freundlich, and Redlich-Peterson). The Avrami equation nicely fitted the kinetic data, while Redlich-Peterson precisely predicted the isotherm data with R^2 values of 0.9987 and 0.9932, respectively. The thermodynamic investigation revealed a negative value of ΔG , ΔH , and ΔS properties, suggesting an exothermic favorable adsorption. The regeneration studies displayed excellent performance of the developed adsorbents, with a minor reduction after five adsorption-desorption cycles, confirming their stability and applicability in practical settings. Overall, this study promised that metal-based ZIF material (such as ANTs@ZIF-8 and ANTs@ZIF-67) would be an attractive adsorbent for the removal of dyes and pharmaceuticals from contaminated water bodies.

7.2 Recommendation

Accordingly, the outcomes reported in this research suggest the potential utilization of metal-based MOF materials for water purification. As an example, aluminum nanotube-based ZIFs demonstrate many attractive features, including a high surface area of ZIFs and the good thermal and chemical stability of aluminum. These combinations promise the ANTs-based ZIF as an appropriate choice for use in water treatment applications. However, the use of these adsorbents is still on a lab scale. There is an obvious need to

evaluate the practical process challenges experienced when using ANT composites, including industrial scale, cost-effective preparation, and reusability.

More research is required to determine the possible risks of ANT composites to human health and ecosystems. A large-scale synthesis approach should be investigated to produce a commercial quantity. Additionally, ANT composites have been investigated primarily for specific pollutants, such as dyes and pharmaceuticals. Evaluating the efficacy of these compounds in wastewater with several harmful contaminants is crucial for advancing research towards practical applications. Furthermore, many studies have reported the successful elimination of contaminants from water using ZIFs. However, there is a lack of research on the use of ANT-based MOFs for this purpose. Therefore, further studies must be conducted to evaluate the efficacy of these adsorbents for water purification.

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