

Phenol-Formaldehyde/Pyrazole Composite: Synthesis, Characterization, and Evaluation of its Chromate Removal Efficiency

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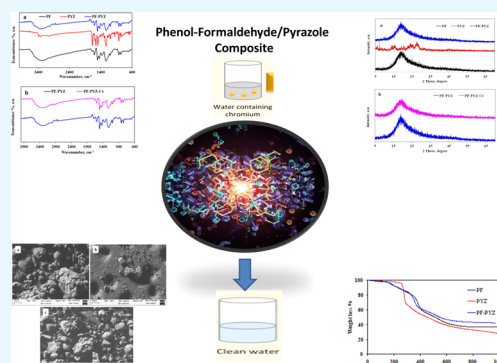
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ABSTRACT: In this study, we report the successful synthesis of a phenol-formaldehyde-pyrazole (PF–PYZ) compound through the surface functionalization of phenol-formaldehyde (PF) with pyrazole (PYZ). The resulting mixture was subjected to comprehensive characterization using a range of analytical techniques, including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The newly synthesized PF–PYZ material effectively removes Cr(VI) ions. Notably, a substantial elimination efficiency of 96% was achieved after just 60 min of contact time. The strategic incorporation of pyrazole (PYZ) as the principal functionalizing agent contributed to this exceptional performance. Notably, the functionalized PYZ sites were strategically positioned on the surface of PF, rendering them readily accessible to metal ions. Through rigorous testing, the optimal sorption capacity of PF–PYZ for Cr(VI) ions was quantified at 0.872 mmol Cr(VI)/g, highlighting the material's superior adsorption capabilities. The practical utility of PF–PYZ was further established through a reusability test, which demonstrated that the chromate capacity remained remarkably stable at 0.724 mequiv Cr(VI)/g over 20 consecutive cycles. This resilience underscores the robustness of the resin, indicating its potential for repeated regeneration and reuse without a significant capacity loss. Our work presents a novel approach to functionalizing phenol-formaldehyde with pyrazole, creating PF–PYZ, a highly efficient material for removing Cr(VI) ions. The compound's facile synthesis, exceptional removal performance, and excellent reusability collectively underscore its promising potential for various water treatments, especially oil field and environmental remediation applications.



1. INTRODUCTION

Industrial processes in the production of automobiles, metal plating, chemicals, electronics, and textiles all contribute to releasing heavy metals into the environment.¹ Diseases like cancer and anemia are just the tip of the iceberg regarding the effects of drinking water contaminated with heavy metals on the nervous, immunological, and respiratory systems.² There are two stable forms of the common toxic metal chromium (Cr) in water: Cr(III) and Cr(VI).³ Cr(III) is a trace element the body needs in comparatively small amounts.³ As the solubility of Cr(VI) in drinking water rises, its potential to cause cancer and gastrointestinal ulcers increases due to enhanced active transport across biological membranes.⁴ The mining,⁴ manufacturing,⁵ electroplating,⁴ and leather industries⁶ all contribute to the massive amounts of Cr(VI) effluent that pollute the environment and lead to an alarming accumulation of Cr(VI) in the biosphere.

Wastewater containing Cr(VI) and other metal ions has been subject to various treatments, such as carbon treatment,⁷ filtration by membrane,⁸ chemical precipitation,⁹ ion exchange,¹⁰ and adsorption.¹¹ Regarding Cr(VI) removal,¹² low

cost,¹³ absence of secondary contamination,¹⁴ and adaptability of operation, adsorption is considered the best alternative technique for eliminating Cr(VI). Although pH, temperature, and pollutant concentration affect the efficiency and cost-effectiveness of the adsorption process, the adsorbent chosen is essential.¹⁵ Activated carbon,¹⁶ metaloxides,¹⁷ polymers,¹⁸ and composites¹⁹ are only some of the many materials studied as potential adsorbents for the chemical and/or physical treatment of Cr(VI). In contrast, polymer adsorbent structure-design ability with highly rich functional group content of –OH, –NH₂, and –COOH makes for many desirable characteristics when treating wastewater. These include a fast adsorption rate,²⁰ ease of handling operation,²¹ and high adsorption capacity with higher metal selectivity.^{22,23}

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Pyrazole compounds are preferred as mono- or bidentate ligands because they can align with heavy metals through two centers and two adjacent N atoms.^{24–26} It was found that this type of molecule can form powerful adsorbents with intriguing qualities, including high selectivity absorption, stability, chemical derivatization, eco-friendliness, biodegradability, and harmlessness to living beings.^{27–30}

The main objective of this article is to develop a new and effective adsorbent material for removing Cr(VI) from aqueous solutions. The researchers prepared a nanocomposite material by combining phenol-formaldehyde (PF) resin with pyrazole (PYZ) to achieve this aim. The characterization of the PF–PYZ nanocomposite was carried out using various techniques such as scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and X-ray diffraction (XRD) to determine its physical and chemical properties. Moreover, the kinetics, isotherm, and thermodynamics of Cr(VI) adsorption onto the PF–PYZ nanocomposite were studied in detail. The kinetics of the adsorption process were analyzed to determine the adsorption rate and the equilibrium time required for maximum adsorption. The isotherm study was carried out to determine the nanocomposite adsorption capacity, and the thermodynamics were investigated to determine the energy changes during the adsorption process.

Furthermore, the effect of pH on the adsorption process was also examined to understand the adsorption mechanism of the PF–PYZ nanocomposite. The researchers assessed the impact of different pH values on the adsorption efficiency of the nanocomposite. They analyzed the effect of pH on the surface charge of the nanocomposite and the speciation of Cr(VI) ions in the solution. This study aims to develop a novel nanocomposite material with a high adsorption capacity for Cr(VI) and to investigate the adsorption mechanism and factors influencing the adsorption process, which could be helpful in developing effective strategies for treating wastewater contaminated with heavy metals.

2. EXPERIMENTAL SECTION

2.1. Materials and Reagents. Phenol crystals (Aldrich, 99%), commercial formaldehyde 37% as an aqueous solution, sodium hydroxide, hydrochloric acid, nitric acid, and oxalic acid (98%) were used. The Cr(VI) working solution was prepared from a stock solution (100 mg L⁻¹) generated from potassium dichromate (grade analytical).

2.2. Methods. **2.2.1. Synthesis of Phenol-Formaldehyde/Pyrazole Composite.** Approximately 2 mmol of phenol, 1.7 mol of formaldehyde (37%), and 0.5 mol of oxalic acid were meticulously mixed at room temperature (RT) for 30 min. Subsequently, the mixture was heated at 100 °C for 4h under reflux conditions with continuous stirring. An additional 0.2 mol of NaOH was introduced, and the reaction mixture was dehydrated under reduced pressure for 60 min. The temperature was gradually raised from 100 to 150 °C during this phase.³¹ It is noteworthy that our prior methodology, as documented in refs 32–34, was employed to synthesize the specified chemical, pyrazole (PYZ).

For the preparation of the composite, approximately 1 g of the prepared phenol-formaldehyde (PF) was dissolved in 7 mL of acetone, and concurrently, 0.75 g of PYZ was introduced into the mixture. The combined solution was subjected to reflux conditions for 1 h. The resulting PF–PYZ resin exhibited an orange hue upon cooling. The composite was

subsequently washed with distilled water and stored at room temperature (RT).

To ascertain the ion exchanger capacity of PF–PYZ, a measured quantity of 0.1 g of the composite was introduced into 100 mL of a solution containing 100 mg L⁻¹ Cr(VI) chloride. The mixture was stirred overnight while maintaining a pH of 5.5 through the judicious use of NaOH and HCl solutions. Following this, the suspension underwent filtration, and the capacity was determined by assessing the reduction in metal concentration within the filtrate.

2.2.2. Optimization of the Batch-Adsorption Process of Cr(VI) on PF–PYZ. During the pH experiment, with stirring, 100 mg of PF–PYZ was suspended in 50 mL of 100 mg L⁻¹ of Cr(VI) at controlled pH values of 2, 5, and 8. The suspension filtrates were acidified with 0.2 mL of HNO₃ to prevent leftover metal ions from precipitating hydroxides. Then, atomic absorption spectroscopy (AAS) was used to determine the total chromium concentration in the filtrates, which was considered the Cr(VI) concentration.

The removal efficiencies (E , %) of the metal ions were calculated using the following equation

$$E = C_i - C_f / C_i * 100\% \quad (1)$$

where C_i is the initial ion concentration and C_f is the final ion concentration.

The distribution coefficient (K_d) is determined using the equation

$$K_d = \frac{C_{i,ex} (\mu\text{g g}^{-1})}{C_{sol} (\mu\text{g mL}^{-1})} \text{mL g}^{-1} \quad (2)$$

where $C_{i,ex}$ is the concentration in the solid phase and C_{sol} is the metal ion concentration in the solution phase.

All subsequent investigations used the optimum circumstances (pH = 8 ± 0.1 and length of stirring = 60 min) to determine how changing the stirring time affected the performance.

0.2 g of PF–PYZ resin was mixed with 25 μg mL⁻¹ in 100 mL of water at the optimal pH and stirring time to examine the wastewater background's potential interference (ions). Filtrates were collected from the solutions, and AAS read the chromium concentration.

2.2.3. Loaded Metal Ions Recovery. The recovery of the loaded metal ions on PF–PYZ was investigated at the optimal pH and stirring duration by mixing 0.2 g in 100 mL of 25 g mL⁻¹ of Cr(VI). Chromium was eluted from the loaded resin by washing it with distilled water and adding 25 mL of 0.1, 0.5, or 1 mol L⁻¹ HCl. The eluates were then subjected to AAS testing. Moreover, eluents of EDTA at 0.001, 0.002, and 0.01 mol L⁻¹ were studied at room temperature and 65 °C with and without 0.1 mol L⁻¹ HCl.

2.2.4. Application to Wastewater Samples. The methodology used in these experiments for application to wastewater samples is as follows:

An effluent sample of 5L of oil field wastewater was collected from Egypt. In preparation for atomic absorption spectroscopy (AAS) analysis, the material underwent an initial filtration step using a sintered glass G4 to eliminate any solid particles or debris. In the next step, the filtered sample volume was carefully adjusted to 100 mL in preparation for analysis. This was done by diluting the sample if the volume exceeded 100 mL or concentrating it by evaporation if the volume was less than 100 mL.

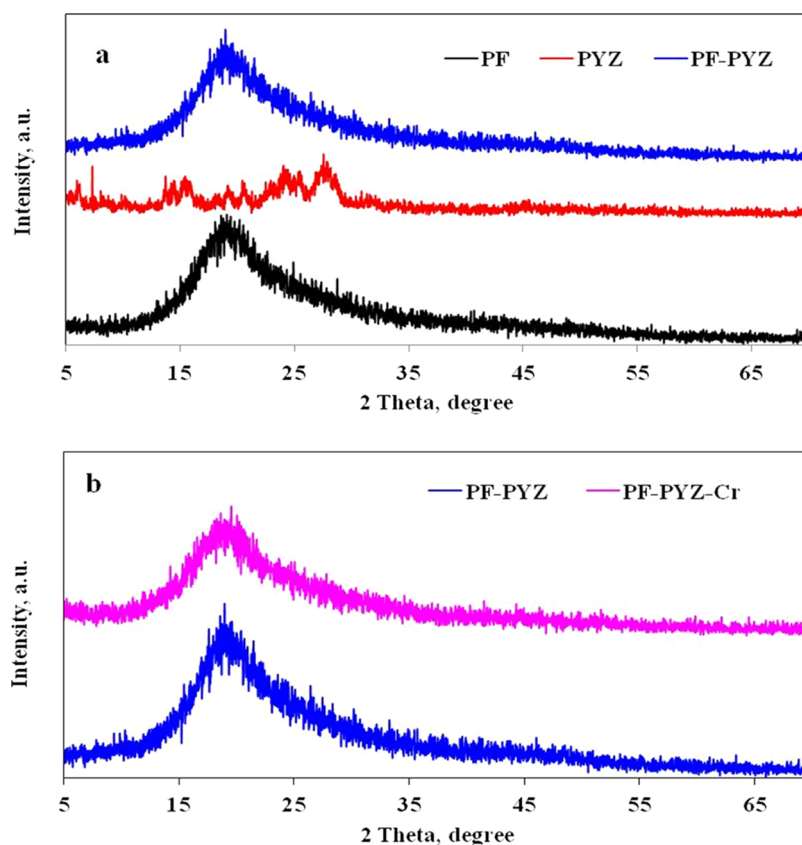


Figure 1. XRD patterns of (a) PF, PYZ, and PF-PYZ and (b) PF-PYZ compared with PF-PYZ-Cr.

In the next step, 0.1 g of PF-PYZ, the ion exchanger, was added to a 100 mL wastewater sample. The pH of the mixture was carefully maintained at 8 ± 0.1 using dilute NaOH or HCl solutions for appropriate pH adjustment. The sample and ion exchanger mixture was stirred for 60 min to ensure sufficient contact and interaction between the ion exchanger and the chromium in the wastewater.

After the 60 min stirring period, the mixture was filtered again to separate the ion exchanger from the solution. The filtrate obtained from this process was collected for further analysis. For a thorough chromium removal and precise determination, the pH of the filtrate was readjusted, and the sample was stirred for an additional 60 min. Finally, another 0.1 g of the ion exchanger, PF-PYZ, was added to the adjusted filtrate. The sample and ion exchanger mixture was stirred for 60 min to allow for further adsorption of any remaining chromium ions. The chromium concentration in the second process filtrate was then determined using AAS, a widely used analytical technique for elemental analysis.

2.3. Characterization. The PF-PYZ was exposed to a powder XRD Shimadzu XRD-6000 to determine the crystallographic pattern. FTIR spectra were recorded on an FT/IR-6800 FTIR spectrometer, Jasco, Japan, by using a KBr pellet. SEM images analyzed the surface texture via a JSM-IT800 Schottky Field Emission Scanning Electron Microscope. Accelerating voltage was 30 kV, and the samples were coated before analysis. TGA was carried out using a TGA-50/50H thermogravimetric analyzer (Micro) from Shimadzu. Heating rate was $10\text{ }^{\circ}\text{C min}^{-1}$ under air. For metal ion analysis, FAAS-4530 was used to detect the residual concentration of chromium. For each measurement, the results are in triplicate.

3. RESULTS AND DISCUSSION

3.1. Characterization of PF-PYZ. The structural, morphological, and thermal stability features of phenol-formaldehyde (PF), pyrazole (PYZ), and functionalized phenol-formaldehyde by pyrazole compound (PF-PYZ) were tested by XRD, FTIR, SEM, and TGA analysis.

3.1.1. Structural Analysis by XRD. The X-ray diffraction (XRD) analyses provide insights into the structural characteristics of the samples under investigation, revealing distinct crystalline phases. Figure 1 displays the XRD patterns for PF, PYZ, PF-PYZ, and PF-PYZ-Cr.

Upon observing the XRD pattern of PF (Figure 1a), it is evident that the broad peak spanning the 2θ range of $13.47\text{--}27.11^{\circ}$ signifies its amorphous nature. Conversely, the XRD pattern of PYZ (Figure 1a) exhibits faint, distinct peaks at $6.22, 15.44, 19.21, 20.61, 24.24, 25.51,$ and 27.63° , indicative of its lower crystallinity. This observation aligns with the structural properties of PYZ.

Interestingly, a semblance between the XRD pattern of the PF-PYZ compound (Figure 1a) and that of the pure PF sample emerges, marked by a comparable broad peak in the same diffraction angle range. This suggests the presence of short-range orders within the synthesized PF-PYZ compound and reaffirms its amorphous nature, similar to PF.^{35,36} Comparative XRD analysis of the PF-PYZ compound before and after chromium adsorption onto PF-PYZ-Cr (Figure 1a,b) reveals no discernible distinctions. This lack of differentiation implies that adsorption occurred at the active surface sites of the PF-PYZ compound, emphasizing the interaction's specificity.

3.1.2. *Structural Analysis by FTIR.* Figure 2a shows the FTIR spectrum of the Novolac resin (PF). It is possible to see

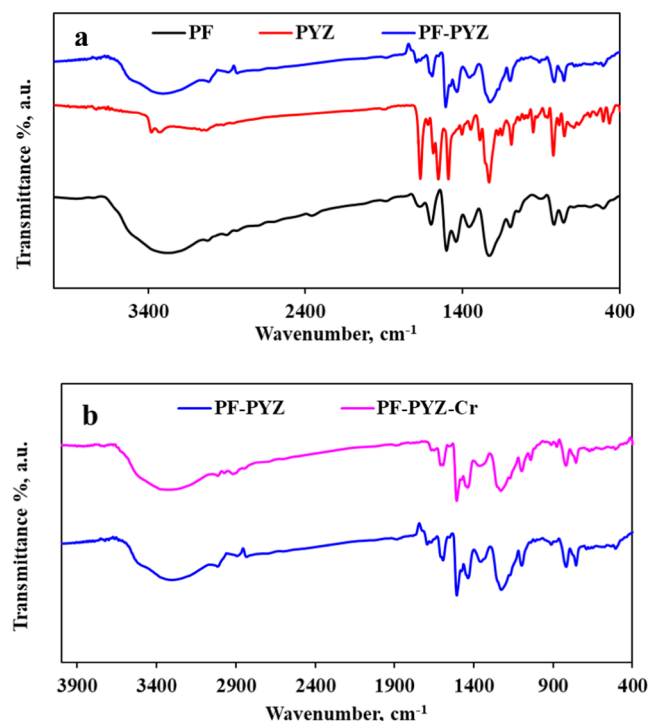


Figure 2. FTIR spectra of (a) PF, PYZ, and PF-PYZ and (b) PF-PYZ compared with PF-PYZ-Cr.

the C–H stretching vibration bands at 2924 and 3000 cm^{-1} .^{37,38} The $\nu_{\text{ph-O}}$ strong band is noticeable at about 1252 cm^{-1} . Bands at 752 cm^{-1} are characteristic of the Novolac family. An 819 cm^{-1} peak represents the bending of the ring C–H bonds of the aromatic ring and bands at 911 cm^{-1} (asymmetric ring stretching in which C–C stretches during contraction of the C–O bond).³⁹ The stretching of –OH, the bending of molecular H_2O , the stretching of C–C in the C_6 ring (doublet), and the Ph-O vibrations, respectively, are attributed to the bands at 3100–3650, 1645, 1612, 1513, and 1107 cm^{-1} . The new resin and phenol-formaldehyde showed a wide broadband at 3400 cm^{-1} related to –OH and –NH groups, and the absorptions at 1600 and 1510 cm^{-1} correspond to the aromatic ring vibrations. The new resin appeared in new bands at 1689, 1551, and 1327 cm^{-1} , mainly attributed to C=C (aliphatic), N=N, and C–N absorption, and the disappearance of peaks at 2899, 2363 cm^{-1} related to CH (aliphatic). The absorption band at 1669 cm^{-1} attributed to the carbonyl group in the ligand disappeared in the new resin; this indicates a condensation reaction between phenol-formaldehyde and ligand.⁴⁰ Figure 2a,b shows the FTIR spectra of PF-PYZ before and after the adsorption. The band at 668 cm^{-1} is assigned to the Cr–O bond after chelating Cr(VI).^{41–44} Because of the interplay between hydroxyl groups in phenols and Cr(VI), a second shoulder band emerged at 1031 cm^{-1} .⁴⁴

3.1.3. *Morphological Analysis by SEM.* The surface morphological features of PF, PYZ, and PF-PYZ were further confirmed by the SEM surface texture in Figure 3a–c. The SEM (Figure 3a) showed that PF has a rough and irregular microstructure morphology with some obvious blocks on the surface. The PYZ compound has a plain, smooth, and uniform

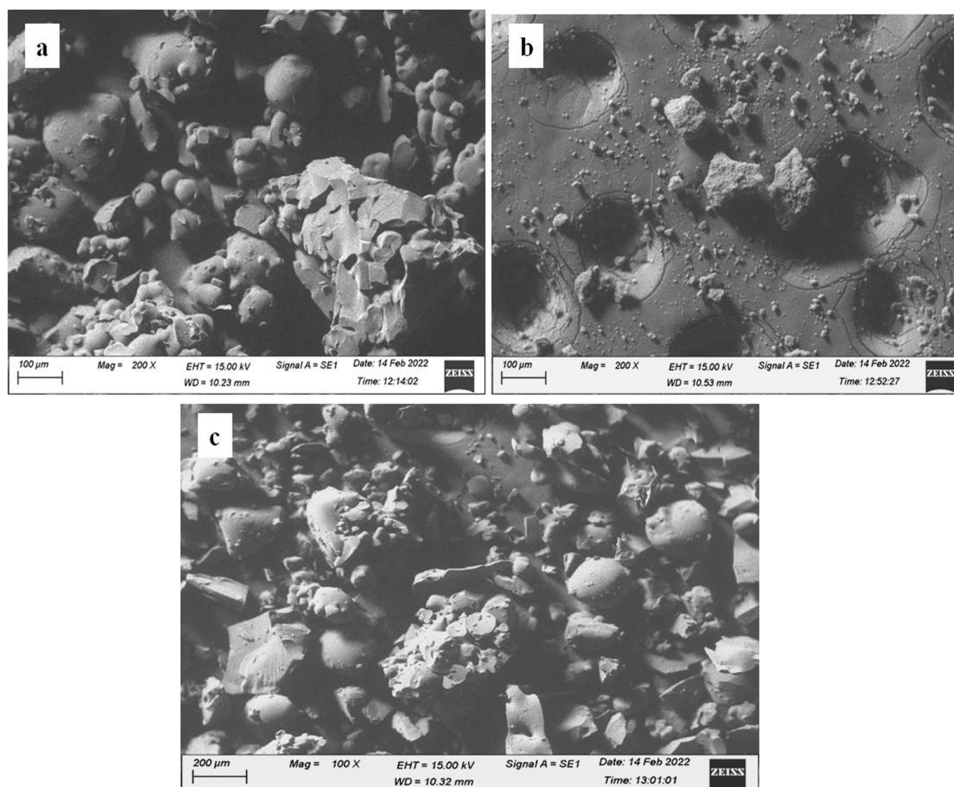


Figure 3. SEM of (a) PF, (b) PYZ, and (c) PF-PYZ samples.

surface, with some fragments of different sizes dispersed on the surface (Figure 3c). In contrast, the PF–PYZ sample displayed a rough external surface (Figure 3c). This new morphology combined with the mentioned PYZ morphology mixed with the PF irregular microstructure but with more scattered fragments of sizes smaller than those of PF, which may be due to the hybridization of PF by PYZ.

3.1.4. Thermal Stability. The thermal stability of PF, PYZ, and PF–PYZ compounds was accelerated throughout their thermogravimetric analysis techniques. The TGA thermographs are listed in Figure 4. PF and PF–PYZ compounds

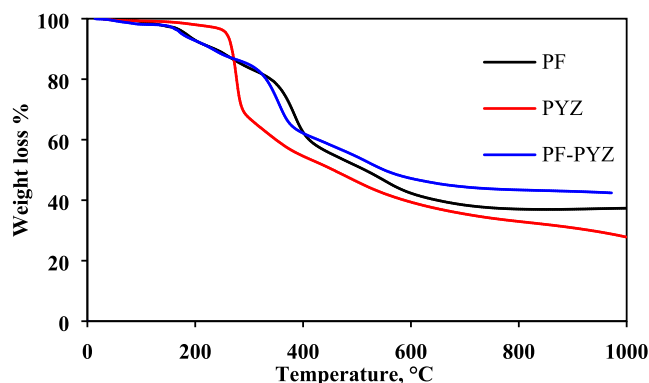


Figure 4. TGA thermographs of PF, PYZ, and PF–PYZ compounds.

exhibit similar thermal behavior trends (Figure 4). The 3.6% initial mass loss up to 142 °C was ascribed to the dehydration of water molecules followed by gradual decomposition due to the different organic working groups' degradation with the production of volatile degradation products. While the PYZ compound exhibits excellent stability up to 230 °C, when the temperature exceeds 230 °C, the structure decomposes gradually with a temperature increase. The PF–PYZ-functionalized compound shows the highest thermal stability among the mentioned compounds, which was thermally stable up to 567 °C.

3.2. Adsorptive Characteristics of PF–PYZ. The adsorptive characteristics of PF–PYZ were evaluated, and the experimental data support the observations made. The adsorption capacity of PF–PYZ for Cr(VI) at pH 8.0 was found to be 0.872 mmol Cr(VI)/g. Although this value is lower than initially expected, it is higher than the theoretical aminogroup capacity of 0.461 mmol Cr(VI)/g. The lower-than-expected capacity can be attributed to the presence of phenolic OH groups within the tunnels and pores of the resin. These OH groups create size restrictions that prevent Cr(VI) ions from accessing them effectively. However, it is important to note that the phenolic OH groups are still accessible to H⁺ ions. This accessibility may explain why the measured capacity is higher than the theoretical capacity based on amino groups alone. Therefore, it can be inferred that both the amino groups and some of the surface-located phenolic OH groups contribute to the metal sorption capacity of PF–PYZ.

3.3. Optimization of the Batch Condition of Cr(VI) on PF–PYZ. **3.3.1. Impact of pH.** The distribution of metal ions between PF–PYZ and the solution is referred to as the distribution coefficient (K_d , cm³/g), and the adsorption concerning the initial concentration of the metal ions (%) of Cr(VI) was determined at pH 2–8 (Figure 5). More Cr(VI) is observed to be adsorbed at higher pH levels. This can be

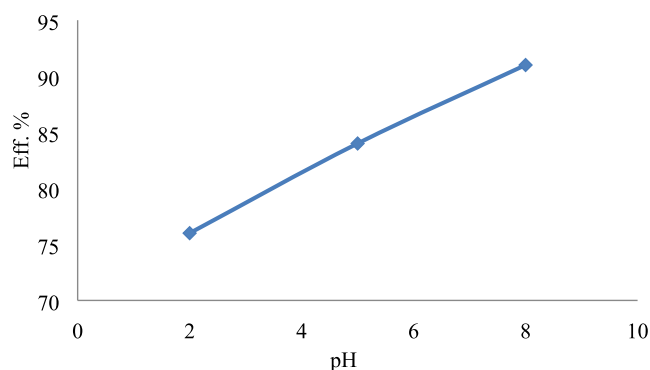


Figure 5. pH effect on the K_d and adsorption (%) of Cr(VI) on 100 mg of PF–PYZ using a stirring time of 10 min.

attributed to the presence of amino and phenolic groups in PF–PYZ, which may enhance the binding of metal ions and prevent their precipitation as hydroxides.^{45,46}

After only 10 min of stirring, the metal ion was effectively extracted. Since Cr(VI) adsorption is thought to be most effective at a pH of 8, that value was selected for further analysis. The optimal pH of 8.0 for Cr(VI) removal observed in this study is unexpected because Cr(VI) is typically retained in strong acid media with a pH range of 2–3. However, it is important to note that the adsorption behavior of Cr(VI) depends on the type of adsorbent material used and the specific conditions of the adsorption process.

In the case of PF–PYZ, the unexpected optimal pH of 8.0 for Cr(VI) removal may be attributed to the unique properties of the nanocomposite material, including its surface charge and chemical composition. The nanocomposite contains amino groups that can act as proton acceptors in basic conditions, which may facilitate the adsorption of Cr(VI) ions at a higher pH. The phenolic OH groups present in the material could also play a role in the adsorption process.

Furthermore, the behavior of Cr(VI) in aqueous solutions is highly complex. It can be influenced by various factors, such as the presence of other ions, the concentration of Cr(VI), and the pH of the solution. Therefore, the unexpected optimal pH of 8.0 for Cr(VI) removal observed in this study may be due to a combination of these factors interacting with the unique properties of the PF–PYZ nanocomposite. While the optimal pH of 8.0 for Cr(VI) removal is not typical, it can be explained by the unique properties of the PF–PYZ nanocomposite and the complex behavior of Cr(VI) in aqueous solutions. Further research is needed to fully understand the underlying mechanisms of the Cr(VI) adsorption behavior on different adsorbent materials under various conditions.

The behavior of increased Cr(VI) adsorption at higher pH levels can be explained by several factors:

- **Surface charge:** At higher pH levels, the surface of the adsorbent material, in this case, PF–PYZ, may become more negatively charged. Cr(VI) ions, which are positively charged species in acidic solutions, are attracted to the negatively charged surface of the adsorbent. This electrostatic attraction facilitates the adsorption of Cr(VI) onto the material.
- **Speciation of Cr(VI):** The speciation of Cr(VI) in aqueous solutions varies with pH. At higher pH values, Cr(VI) exists predominantly in the form of anionic species, such as chromate (CrO_4^{2-}) and hydrogen chromate (HCrO_4^-). These anionic species have a

higher affinity for positively charged sites on the adsorbent surface, thereby increasing the adsorption of Cr(VI) at higher pH levels.

- **Complexation reactions:** The presence of amino groups in PF–PYZ can act as proton acceptors in basic conditions. These amino groups can form complexes with Cr(VI) ions, enhancing adsorption. The complexation reactions between the amino groups and Cr(VI) ions are more favorable at higher pH levels, leading to increased adsorption.
- **Precipitation avoidance:** At higher pH levels, the formation of metal hydroxides, such as chromium hydroxide ($\text{Cr}(\text{OH})_3$), is minimized. The amino and phenolic groups in PF–PYZ can bind to Cr(VI) ions, preventing their precipitation as hydroxides. This allows more Cr(VI) to remain in the solution and be adsorbed onto the adsorbent material.

3.3.2. Effect of Stirring Time. In the actual use of waste treatment, the equilibration time is a significant aspect. Hence, the optimal pH of 8.0 is used to study the impact of stirring time on the effectiveness of the adsorption process onto PF–PYZ (Figure 6). 1 h of stirring is enough to reach a maximum

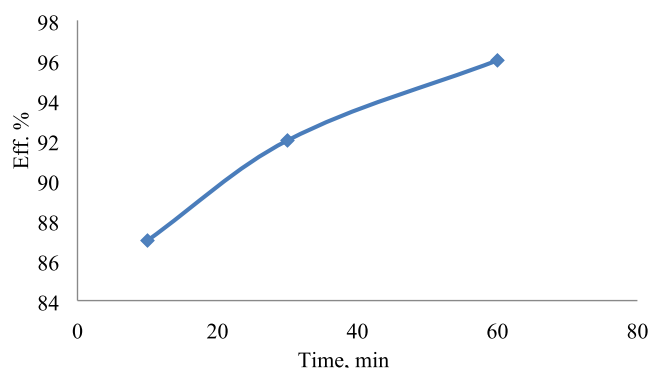


Figure 6. Stirring time affects the adsorption process at pH 8.0.

adsorption of 96%. It can be inferred that PF–PYZ has faster kinetics with larger capacities when compared to the equilibration times and adsorption efficiencies reported elsewhere utilizing PF functionalized with $-\text{SO}_3\text{H}/-\text{COOH}$ acids, *o*-aminophenol/dithioxamide, or Schiff bases of *o*-phenylenediamine with *o*-, *m*-, and *p*-hydroxybenzaldehydes. The principal functionalizing agent, PYZ, is found on the outer layer of PF, where it may be readily accessed by the metal ions, which may explain this phenomenon. Surface-modified PYZ materials are well known to exhibit such rapid kinetics.^{47–50}

3.3.3. Effect of Interference Ions. The study investigated the influence of chloride and sulfate ions on the adsorption effectiveness of Cr(VI) on PF–PYZ. The experimental data revealed that the presence of chloride or sulfate ions in water did not significantly affect the adsorption capacity of PF–PYZ for Cr(VI). The data presented in Table 1 demonstrates that chloride or sulfate ions in the water had minimal impact on the adsorption effectiveness of PF–PYZ for Cr(VI). In all cases, a significant reduction in the Cr(VI) concentration was achieved, indicating that PF–PYZ can effectively adsorb Cr(VI), even in the presence of interference ions. The specific functional groups on the surface of the PF–PYZ nanocomposite, such as amino and phenolic groups, provide selective binding sites for Cr(VI) ions. The presence of chloride and sulfate ions does not significantly interfere with

Table 1. Effect of Interference Ions on Cr(VI) Adsorption by PF–PYZ

interference ions	initial Cr(VI) concentration(mg/L)	final Cr(VI) concentration after adsorption(mg/L)
no interference	50	0.5
chloride ions	50	0.6
sulfate ions	50	0.4

the interaction between Cr(VI) and these functional groups on the adsorbent surface.

3.4. Recovery of Adsorbed Metal Ions. The recovery of adsorbed metal ions is a critical aspect of the adsorption process, as it determines the reusability and cost-effectiveness of the adsorbent material. In recent years, there has been a growing interest in developing adsorbent materials that are stable and effective and can be easily regenerated for multiple uses. Various studies have investigated the use of different eluents and temperatures for the recovery of the adsorbed metal ions. For instance, chemicals such as HCl, EDTA, NaOH, and others have been employed as eluents to recover heavy metal ions from different adsorbent materials. The choice of eluent depends on factors such as the type of adsorbent material, the nature of the metal ion, and the specific conditions of the adsorption process.

Due to its strong complexing ability, EDTA is commonly used as a chelating agent for recovering heavy metal ions from adsorbent materials. It forms stable complexes with metal ions, allowing easy desorption from the adsorbent material when EDTA is used as an eluent. Numerous studies have reported the use of EDTA as an eluent for the recovery of metal ions, including Cr(VI), Pb(II), Cu(II), and others.⁵¹ The stability and reusability of adsorbent materials are crucial in developing practical and sustainable methods for removing heavy metal ions from aqueous solutions. The ability to regenerate the adsorbent material for multiple uses can significantly reduce the cost and environmental impact of the treatment process.

In this study, the PF–PYZ nanocomposite demonstrated good stability and reusability. It could be effectively regenerated using EDTA as an eluent (Table 2). The capacity

Table 2. Impact of EDTA and HCl Concentrations on the Recovery Rate (%) [Cr(VI) Volume 100 mL, Concentration 25 g mL⁻¹, Dose 0.2 PF–PYZ, pH 8.0, and Stirring Time 60 min]

eluent	Cr(VI) %
HCl 0.1 mol L ⁻¹	8.4
HCl 0.5 mol L ⁻¹	9.1
HCl 1.0 mol L ⁻¹	6.2
0.1 mol L ⁻¹ HCl + EDTA 0.001 mol L ⁻¹	9.6
0.1 mol L ⁻¹ HCl + EDTA 0.002 mol L ⁻¹	59.7
0.1 mol L ⁻¹ HCl + EDTA 0.001 mol L ⁻¹ at 65 °C	53.4
0.1 mol L ⁻¹ HCl + EDTA 0.01 mol L ⁻¹	87.8
0.1 mol L ⁻¹ HCl + EDTA 0.01 mol L ⁻¹ at 65 °C	91.3

of the nanocomposite for Cr(VI) did not significantly change even after repeating 20 cycles of metal ion separation and elution processes using 0.01 mol L⁻¹ EDTA as an eluent, indicating the stability and reusability of the resin. Therefore, the recovery of the adsorbed metal ions is a crucial aspect of the adsorption process. Developing effective and sustainable methods for the recovery and reusability of adsorbent materials

is essential for the efficient and cost-effective treatment of heavy metal ions in aqueous solutions.

3.5. Application to Electroplating Workshop Wastewater Effluents. In particular, this research intends to examine how effluents from wastewater treatment plants are managed. Large quantities are released from the electroplating workshops. Without pretreatment, wastewater from the workshops is discharged into the municipal sewage system, posing a serious environmental risk. During the working course of two shifts, the workshops release their effluent, averaging 25.5 m³ every day. When the metal has been formed and shaped, it undergoes a series of operations, including dry cleaning, acid washing, rinsing, and Ni–Cr electroplating, for a shiny finish. Hence, the availability of this relatively straightforward technique for dealing with wastewater effluents is crucial.

100 mL of two wastewater effluents were treated using the ideal extraction conditions for Cr(VI) (pH 8.0, 60 min of stirring at room temperature), as shown in Table 3. The remaining metal ions were below the detection limit (0.05 g mL⁻¹). As a result, PF–PYZ could virtually eliminate the heavy metal ions.

Table 3. The Concentration of Cr(VI) in 100 mL of Waste Effluents from an Electroplating Workshop before and after Extraction with 2 × 100 mg PF–PYZ

adsorbate	sample 1		sample 2		permitted amount
	before treatment	after treatment	before treatment	after treatment	
Cr(VI)	12.4 mg/L	0.02 mg/L	11.3 mg/L	0.02 mg/L	0.5 mg/L

4. CONCLUSIONS

In conclusion, this study successfully synthesized and characterized a new adsorbent, PF–PYZ, by surface functionalizing phenol-formaldehyde (PF) with pyrazole (PYZ). The analytical characterization of the PF–PYZ compound using XRD, FTIR, SEM, and TGA techniques confirmed its structural and thermal stability. The PF–PYZ compound demonstrated high efficiency in removing Cr(VI) ions from water with a 96% elimination rate achieved after just 60 min of contact time. The optimal conditions for adsorption were determined to be at a temperature of 298 K, a contact time of 60 min, and a pH of 8. The adsorption mechanism was found to be physisorption, including electrostatic attraction. The optimum sorption quantity of PF–PYZ was determined as 0.872 mmol Cr(VI)/g, which shows that the PF–PYZ compound has a high capacity for the adsorption of Cr(VI) ions. The reusability test showed that the chromate capacity of PF–PYZ did not significantly change (0.724 mequiv Cr(VI)/g) after 20 consecutive cycles, indicating the stability of the resin and its capacity for regeneration and reuse more than once. These findings suggest that the PF–PYZ compound has excellent potential for water treatment as an efficient and reusable adsorbent for the removal of Cr(VI) ions.

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Notes

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DEDICATION

This work is dedicated to the memory of the pure soul of Professor Mohamed Abbas El-Metwally (D.Sc.), who was working at the Department of Chemistry, Faculty of Science, Mansoura University, Egypt.

REFERENCES

- Ihsanullah; Abbas, A.; Al-Amer, A. M.; Laoui, T.; Liang, Z.; Nasser, M. S.; Khraisheh, M.; Atieh, M. A. Heavy Metal Removal from Aqueous Solution by Advanced Carbon Nanotubes: Critical Review of Adsorption Applications. *Sep. Purif. Technol.* **2016**, *157*, 141–161.
- Kim, M. K.; Sundaram, K. S.; Iyengar, G. A.; Gopalan, A. I. A Novel Chitosan Functional Gel Included with Multiwall Carbon Nanotube and Substituted Polyaniline as Adsorbent for Efficient Removal of Chromium Ion. *Chem. Eng. J.* **2015**, *267*, 51–64.
- Zhou, Q.; Yan, C.; Luo, W. Polypyrrole Coated Secondary Fly Ash–Iron Composites: Novel Floatable Magnetic Adsorbents for the Removal of Chromium (VI) from Wastewater. *Mater. Des.* **2016**, *92*, 701–709.
- Zhou, L.; Liu, Y.; Liu, S.; Yin, Y.; Zeng, G.; Tan, X.; Hu, X.; Hu, X.; Jiang, L.; Ding, Y.; Liu, S.; Huang, X. Investigation of the Adsorption-Reduction Mechanisms of Hexavalent Chromium by Ramie Biochars of Different Pyrolytic Temperatures. *Bioresour. Technol.* **2016**, *218*, 351–359.
- Wu, Y.; Yilihan, P.; Cao, J.; Jin, Y. Competitive Adsorption of Cr (VI) and Ni (II) onto Coconut Shell Activated Carbon in Single and Binary Systems. *Water, Air, Soil Pollut.* **2013**, *224* (9), 1662–1–1662–13, DOI: [10.1007/s11270-013-1662-6](https://doi.org/10.1007/s11270-013-1662-6).
- Polowczyk, I.; Urbano, B. F.; Rivas, B. L.; Bryjak, M.; Kabay, N. Equilibrium and Kinetic Study of Chromium Sorption on Resins with

- Quaternary Ammonium and N-Methyl- d -Glucamine Groups. *Chem. Eng. J.* **2016**, *284*, 395–404.
- (7) Babu, B. V.; Gupta, S. Adsorption of Cr(VI) Using Activated Neem Leaves: Kinetic Studies. *Adsorption* **2008**, *14* (1), 85–92.
- (8) El-Sheikh, M. N.; Metwally, B. S.; Fathy, M.; Ahmed, H. B.; Moghny, Th. A.; Zayed, A. I. Fabrication of Electrospun Polyamide–Weathered Basalt Nano-Composite as a Non-Conventional Membrane for Basic and Acid Dye Removal. *Polym. Bull.* **2022**, *80*, 8511–8533, DOI: 10.1007/s00289-022-04459-w.
- (9) Zhang, K.; Li, H.; Xu, X.; Yu, H. Facile and Efficient Synthesis of Nitrogen-Functionalized Graphene Oxide as a Copper Adsorbent and Its Application. *Ind. Eng. Chem. Res.* **2016**, *55* (8), 2328–2335.
- (10) Kahu, S.; Shekhawat, A.; Saravanan, D.; Jugade, R. Two Fold Modified Chitosan for Enhanced Adsorption of Hexavalent Chromium from Simulated Wastewater and Industrial Effluents. *Carbohydr. Polym.* **2016**, *146*, 264–273.
- (11) Fathy, M.; Zayed, A. I.; Ahmed, H. B. Activated Carbon/Carborundum@Microcrystalline Cellulose Core Shell Nano-Composite: Synthesis, Characterization and Application for Heavy Metals Adsorption from Aqueous Solutions. *Ind. Crops Prod.* **2022**, *182*, No. 114896.
- (12) Ahmed, H. A.; Soliman, M. S.; Othman, S. A. Synthesis and characterization of magnetic nickel ferrite-modified montmorillonite nanocomposite for Cu (II) and Zn (II) ions removal from wastewater. *Egypt. J. Chem.* **2021**, *64* (10), 5627–5645.
- (13) Crini, G. Non-Conventional Low-Cost Adsorbents for Dye Removal: A Review. *Bioresour. Technol.* **2006**, *97* (9), 1061–1085.
- (14) Kim, I. Y.; Lee, J. G.; Hwang, E. J.; Pei, Y.-R.; Jin, W. B.; Choy, J.-H.; Hwang, S. J. Water-Floating Nanohybrid Films of Layered Titanate–Graphene for Sanitization of Algae without Secondary Pollution. *RSC Adv.* **2016**, *6* (100), 98528–98535.
- (15) Bădescu, I. S.; Bulgariu, D.; Ahmad, I.; Bulgariu, L. Valorisation possibilities of exhausted biosorbents loaded with metal ions—a review. *J. Environ. Manage.* **2018**, *224*, 288–297.
- (16) Ocampo-Pérez, R.; Aguilar-Madera, C. G.; Díaz-Blancas, V. 3D Modeling of Overall Adsorption Rate of Acetaminophen on Activated Carbon Pellets. *Chem. Eng. J.* **2017**, *321*, 510–520.
- (17) Wang, J.; Tang, H.; Zhang, L.; Ren, H.; Yu, R.; Jin, Q.; Qi, J.; Mao, D.; Yang, M.; Wang, Y.; Liu, P.; Zhang, Y.; Wen, Y.; Gu, L.; Ma, G.; Su, Z.; Tang, Z.; Chen, C.; Wang, D. Multi-Shelled Metal Oxides Prepared via an Anion-Adsorption Mechanism for Lithium-Ion Batteries. *Nat. Energy* **2016**, *1* (5), No. 16050, DOI: 10.1038/energy.2016.50.
- (18) Min, Y.; Hammond, P. T. Catechol-Modified Polyions in Layer-by-Layer Assembly to Enhance Stability and Sustain Release of Biomolecules: A Bioinspired Approach. *Chem. Mater.* **2011**, *23* (24), 5349–5357.
- (19) Mager, E. M.; Pasparakis, C.; Schlenker, L. S.; Yao, Z.; Bodinier, C.; Stieglitz, J. D.; Hoening, R.; Morris, J. S.; Benetti, D. D.; Grosell, M. Assessment of Early Life Stage Mahi-Mahi Windows of Sensitivity during Acute Exposures to DeepwaterHorizonCrude Oil. *Environ. Toxicol. Chem.* **2017**, *36* (7), 1887–1895.
- (20) Sivrikaya, S.; Cerrahoglu, E.; Imamoglu, M.; Arslan, M. 1,3,5-Triazine-Triethylenetetramine Polymer: An Efficient Adsorbent for Removal of Cr(VI) Ions from Aqueous Solution. *Toxicol. Environ. Chem.* **2013**, *95* (6), 899–908.
- (21) Fan, J.; Li, D.; Teng, W.; Yang, J.; Liu, Y.; Liu, L.; Elzatahry, A. A.; Alghamdi, A. A.; Deng, Y.; Li, G.; Zhang, W.-X.; Zhao, D. Ordered Mesoporous Silica/Polyvinylidene Fluoride Composite Membranes for Effective Removal of Water Contaminants. *J. Mater. Chem. A* **2016**, *4* (10), 3850–3857.
- (22) Liu, Y.; Meng, X.-G.; Han, J.; Liu, Z.; Meng, M.; Wang, Y.; Chen, R.; Sujun, T. Speciation, Adsorption and Determination of Chromium(III) and Chromium(VI) on a Mesoporous Surface Imprinted Polymer Adsorbent by Combining Inductively Coupled Plasma Atomic Emission Spectrometry and UV Spectrophotometry. *J. Sep. Sci.* **2013**, *36* (24), 3949–3957.
- (23) Bulgariu, D.; Nemeş, L.; Ahmad, I.; Bulgariu, L. Isotherm and Kinetic Study of Metal Ions Sorption on Mustard Waste Biomass Functionalized with Polymeric Thiocarbamate. *Polymers* **2023**, *15* (10), 2301.
- (24) Metwally, M. A.; Bondock, S.; El-Desouky, S. I.; Abdou, M. M. A Worthy Insight into the Dyeing Applications of AzoPyrazolyl Dyes. *Int. J. Modern Org. Chem.* **2012**, *1* (3), 165–192.
- (25) Metwally, M. A.; Bondock, S. A.; El-Desouky, S. I.; Abdou, M. M. Pyrazol-5-ones: tautomerism, synthesis and reactions. *Int. J. Modern Org. Chem.* **2012**, *1* (1), 19–54.
- (26) Abdou, M. M.; Bondock, S.; El-Desouky, S. I.; Metwally, M. A. Synthesis, spectroscopic studies and technical evaluation of novel disazo disperse dyes derived from 3-(2-hydroxyphenyl)-2-pyrazolin-5-ones for dyeing polyester fabrics. *Am. J. Chem.* **2013**, *3* (3), 59–67.
- (27) Metwally, M. M. M.; Bondock, S.; El-Desouky, E.-S.; Abdou, M. M. A Facile Synthesis and Tautomeric Structure of Novel 4-arylhydrazono-3-(2-hydroxyphenyl)-2-pyrazolin-5-ones and Their Application as Disperse Dyes. *Color. Technol.* **2013**, *129* (6), 418–424.
- (28) Abbas, M. A.; Eid, A.; Abdou, M. M.; Elgendy, A.; El-Saeed, R. A.; Zaki, E. G. Multifunctional Aspects of the Synthesized Pyrazoline Derivatives for AP1 5L X60 Steel Protection Against MIC and Acidization: Electrochemical, In Silico, and SRB Insights. *ACS Omega* **2021**, *6* (13), 8894–8907.
- (29) El-Saeed, R. A.; Hosny, R.; Fathy, M.; Abdou, M. M.; Shoueir, K. R. An Innovative SiO₂-Pyrazole Nanocomposite for Zn(II) and Cr(III) Ions Effective Adsorption and Anti-Sulfate-Reducing Bacteria from the Produced Oilfield Water. *Arabian J. Chem.* **2022**, *15* (8), No. 103949.
- (30) El-Katori, E. E.; El-Saeed, R. A.; Abdou, M. M. Anti-Corrosion and Anti-Microbial Evaluation of Novel Water-Soluble Bis AzoPyrazole Derivative for Carbon Steel Pipelines in Petroleum Industries by Experimental and Theoretical Studies. *Arabian J. Chem.* **2022**, *15* (12), No. 104373.
- (31) Abou-El-Sherbini, K. S.; Nour, M.; Soliman, A.-E.-G.; Elmorsy, S. S. Synthesis of a Novolac-Based 3-Aminopropylsiloxane Resin and Its Application for the Removal of Cu²⁺, Cr³⁺, and Ni²⁺ from Electroplating Wastewater. *J. Appl. Polym. Sci.* **2014**, *131* (131), No. 40993.
- (32) Metwally, M. A.; Bondock, S.; El-Desouky, E.-S.; Abdou, M. M. Synthesis, Structure Elucidation and Application of Some New Azo Disperse Dyes Derived from 4-Hydroxycoumarin for Dyeing Polyester Fabrics. *Am. J. Chem.* **2012**, *2* (6), 347–354.
- (33) (a) Metwally, M. A.; Bondock, S.; El-Desouky, S. I.; Abdou, M. M. Synthesis, Structure Investigation and Dyeing Assessment of Novel Bisazo Disperse Dyes Derived from 3-(2'-Hydroxyphenyl)-1-Phenyl-2-Pyrazolin-5-Ones. *J. Korean Chem. Soc.* **2012**, *56* (3), 348–356. (b) Metwally, M. A.; Bondock, S.; El-Desouky, S. I.; Abdou, M. M. Synthesis, Tautomeric Structure, Dyeing Characteristics, and Antimicrobial Activity of Novel 4-(2-Arylazophenyl)-3-(2-Hydroxyphenyl)-1-Phenyl-2-Pyrazolin-5-Ones. *J. Korean Chem. Soc.* **2012**, *56* (1), 82–91.
- (34) (a) Abdou, M. M.; Gizawy, M. A.; Shamsel-Din, H. A. Green synthesis, radioiodination and in vivo biodistribution of 5-(2-hydroxyphenyl)-2,4-dihydro-3H-pyrazol-3-one derivatives as potential candidates for lung imaging. *Appl. Radiat. Isot.* **2024**, *203*, No. 111096. (b) Shaban, M. M.; El Basiony, N. M.; Radwan, A. B.; El-Katori, E. E.; Abu-Rayyan, A.; Bahtiti, N. H.; Abdou, M. M. Electrochemical investigation of c-steel corrosion inhibition, in silico, and sulfate-reducing bacteria investigations using pyrazole derivatives. *ACS Omega* **2023**, *8* (33), 30068–30080.
- (35) Tamjidi, S.; Moghadas, B. K.; Esmaeili, H. Ultrasound-assisted biodiesel generation from waste edible oil using CoFe₂O₄@GO as a superior and reclaimable nanocatalyst: Optimization of two-step transesterification by RSM. *Fuel* **2022**, *327*, No. 125170.
- (36) Khaleghi, H.; Esmaeili, H.; Jaafarzadeh, N.; Ramavandi, B. Date seed activated carbon decorated with CaO and Fe₃O₄ nanoparticles as a reusable sorbent for removal of formaldehyde. *Korean J. Chem. Eng.* **2022**, *39* (1), 146–160.
- (37) Elbanna, S. A.; Rhman, A. M. M. A. E.; Al-Hussaini, A. S.; Khalil, S. A. Synthesis, Characterization, and Performance Evaluation

of Novel Terpolymers as Pour Point Depressors and Paraffin Inhibitors for Egyptian Waxy Crude Oil. *Pet. Sci. Technol.* **2022**, *40* (18), 2263–2283.

(38) Elbanna, S. A.; Rhman, A. M. M. A. E.; Al-Hussaini, A. S.; Khalil, S. A. Development of Novel Terpolymers and Evaluating Their Performance as Pour Point Depressants and Paraffin Inhibitors for Waxy Crude Oil. *Egypt. J. Chem.* **2023**, *66* (1), 63–72.

(39) Hu, X.; Zeng, J.; Dai, W.-J.; Shi, W.; Li, L.; Han, C. EPDM/Vinyl Triethoxysilane Modified Phenol Formaldehyde Resin Composite. *Polym. Bull.* **2011**, *66* (5), 703–710.

(40) Guo, Z.; Liu, Z.; Ye, L.; Ge, K.; Zhao, T. The Production of Lignin-Phenol-Formaldehyde Resin Derived Carbon Fibers Stabilized by BN Pre-ceramic Polymer. *Mater. Lett.* **2015**, *142*, 49–51.

(41) Dong, K.; Hu, T.; Wei, G.; Liu, Q.; Gao, T.; Zhang, X.; Yao, J. Removal of Hexavalent Chromium from Aqueous Solution Using Novel Dye-Based Adsorbent Prepared by Flocculation. *Sep. Sci. Technol.* **2019**, *54*, 1739.

(42) Hu, T.; Liu, Q.; Liu, Q.; Wu, Y. C.; Qiao, C.; Yao, J. Toxic Cr Removal from Aqueous Media Using Catechol-Amine Copolymer Coating onto as-Prepared Cellulose. *Carbohydr. Polym.* **2019**, *209*, 291–298.

(43) Wu, C. Spectroscopic Studies on Cation-Doped Spinel LiMn₂O₄ for Lithium Ion Batteries. *Solid State Ionics* **2001**, *144* (3–4), 277–285.

(44) Chang, X.; Li, M.; Liu, Q.; Liu, Q.; Yao, J. Adsorption–Reduction of Chromium(vi) from Aqueous Solution by Phenol–Formaldehyde Resin Microspheres. *RSC Adv.* **2016**, *6* (52), 46879–46888.

(45) Ge, Y.; Li, Z. Application of lignin and its derivatives in adsorption of heavy metal ions in water: a review. *ACS Sustainable Chem. Eng.* **2018**, *6* (5), 7181–7192.

(46) Kamel, N. H. M.; Sayyah, A. M.; Abdel-Aal, A. K. Ground Water in Certain Sites in Egypt and Its Treatments Using a New Modified Ion Exchange Resin—Characterization of Water and Modified Ion Exchange. *J. Environ. Prot.* **2011**, *02* (04), 435–444.

(47) Dey, R. K.; Jha, U.; Singh, A. K.; Samal, S.; Ray, A. R. Extraction of Metal Ions Using Chemically Modified Silica Gel Covalently Bonded with 4,4'-Diaminodiphenylether and 4,4'-Diaminodiphenylsulfone-Salicylaldehyde Schiff Bases. *Anal. Sci.* **2006**, *22* (8), 1105–1110.

(48) Abou-El-Sherbini, K. S.; Kenawy, I. M. M.; Issa, R. M. Chemical Modification of Controlled-Pore Silica With N-Propylsalicylaldehyde. *J. Appl. Polym. Sci.* **2003**, *88*, 3159–3167.

(49) Samal, S.; Acharya, S. K.; Dey, R. K.; Ray, A. Synthesis, Characterization, and Metal Ion Uptake Studies of Chelating Resins Derived from Formaldehyde/Furfuraldehyde Condensed Phenolic Schiff Base of 4,4'-Diaminodiphenylmethane Ando-Hydroxyacetophenone. *J. Appl. Polym. Sci.* **2003**, *88* (2), 570–581.

(50) Vallet-Regí, M.; Schüth, F.; Lozano, D.; Colilla, M.; Manzano, M. Engineering Mesoporous Silica Nanoparticles for Drug Delivery: Where Are We after Two Decades? *Chem. Soc. Rev.* **2022**, *51* (13), 5365–5451.

(51) Zhang, K.; Dai, Z.-W.; Zhang, W.; Gao, Q.; Dai, Y.; Xia, F.; Zhang, X. EDTA-Based Adsorbents for the Removal of Metal Ions in Wastewater. *Coord. Chem. Rev.* **2021**, *434*, No. 213809.