

RESEARCH PAPER

Study of Heavy Metal Ions Adsorption Using Grafted Polyurethane with Iron Oxide Nanoparticles as Adsorbent

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ABSTRACT

Adsorption of lead ions Pb (II), Chromium ions Cr (III) and Cadmium ions Cd (II) using the polyurethane grafted on the iron oxide nanoparticles (PU-MNPs) has been investigated in the current study. The adsorbent was characterized using a variability of techniques counting Atomic Absorption Spectroscopy (AAS), Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA and DSC). Different parameters were investigated to obtain the best results such as pH, contact time, the concentration of initial metals and temperature. In regard to the pH parameter, the highest adsorption rates were obtained at pH of 6, 7, and 5 for Pb (II), Cr (III) and Cd (II) respectively. In terms of the contact time, the minimum contact time was 60 min, 30 min and 45 min for Pb (II), Cr (III) and Cd (II) respectively. The initial concentration was 250 mg/g of each studied ion (Pb (II), Cr (III) and Cd (II)). The 300 agitation rpm speed at temperature 25±2 °C. were 70%, 76% and 73% for Lead, Chromium and Cadmium ions respectively. The results showed that the adsorption for the three investigated ions Pb (II), Cr (III) and Cd (II) followed the Lankemere and Freundlich equations., and the maximum adsorption of Cd(II)>Cr(III)>Pb(II).

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INTRODUCTION

Azo dyes are organic compounds consisting of two organic groups linked together via coupling reactions to give colored compounds [1]. Azo dyes may contain one or more assortments of azo dyes, making up more than half of the dyes in use today. They vary in complexity according to the number of auxochrome groups, found there most commercial dyes belong to most commercial dyes to azo dyes due to their flexibility in compounds due to their various applications [2]. Isocyanate is used mainly in the preparation of polyurethane and can be classified into two groups of aromatic substances; Toluene diisocyanate

(TDI) and methylene diphenyl diisocyanate (MDI). Polyurethane is produced by the condensation polymerization reaction between poly Isocyanates and polyols [3]. The reaction between OH alcohol and isocyanate with NCO produces urethane, because water pollution poses fewer direct threats to human health, and many lakes and rivers are polluted. Various methods are used to combat water pollution, such as sedimentation, chemical oxidation, coagulation, aeration, flotation, reverse osmosis, Nanofiltration, chemical precipitation, ion exchange, membrane separation and classification Optical [4,5]. However, adsorption processes are currently one of the most important and effective

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methods for the purification and removal of types of various pollutants in the water.

Numerous processes are applied to remove minerals from water and wastewater. Some of the traditional techniques that have been used to treat industrial wastewater include ion exchange, filtration, chemical precipitation, flotation, and adsorption. Adsorption is the accumulation of different substances in the form of surface molecules, atoms or ions. There are many examples of adsorption, including acetic acid adsorption on animal charcoal, where acidic particles collect on the surface of coal particles, hydrogen adsorption on some metals such as nickel and iron, and gas accumulation. Hydrogen is present in the form of molecules and atoms on the surface of these two metals [6]. In the current study, the factors affecting the adsorption capacity will be investigated, in addition to studying the Langmuir and Freundlich equations for the adsorption of heavy metal ions on modified polyurethane-magnetic nanoparticles (PU-MNPs).

MATERIALS AND METHODS

Materials

All chemical reagents used in the work were analytical high-purity and were used without further purification, including 2-Naphthol (%95, OEM), Sodium hydroxide (%98, THOMAS BAKER), Hydrogen chloride (%37, ROMIL-SA), Chloroform (%99, GCC), Sodium nitrite (99%, B.D.H), Ethanol absolute (%99.9, ROMIL-SA), Methylene diphenyl diamine(%99, HEXION Responsible chemistry), Diphenyl methane diisocyanate (%99.5, Industry Engineering Co. Ltd), Preparation Ions solution by using deionized water, Lead Nitrate (%99, Hunan Sincere Chemicals Co.,Ltd), Chromium Nitrate (%99, CDH), Cadmium Nitrate (%99, Jinan Future Chemical Co.,Ltd), Fe₃O₄ nanoparticles, Methanol (Absolute) (%99.9, Xilong Scientific), N, N-Dimethyl Formamide (%99, CDH).

Preparation of Azo dye and PU-MNPs

0.01 mol of methylene diphenyl diamine was dissolved in (10.00 ml) of concentrated hydrochloric acid, and then (10.00 ml) of distilled water was added with stirring at a temperature of (5-0 °C). A solution was prepared by dissolving (1.104 g) of sodium nitrite (2 mol) in (8 ml) of distilled water with stirring at a temperature of (5-0 °C). The solution prepared was added to the solution prepared above. Slowly drop and drop to

form diazonium salt while maintaining the solution temperature. Another solution was prepared by dissolving 0.01 mol of beta-naphthol in 16ml of 10% sodium hydroxide solution with stirring at a temperature of (5-0 °C). Then add the diazonium salt prepared above slowly with continuous stirring to the solution prepared to form a solution in the form of foam of two colors red with dark and leave the solution in ice for 15 minutes at a temperature of 5 °C. Then the solution is filtered, and a precipitate of a maroon color is formed, then it is left for the next day to dry in the air to complete the coupling process, then the medium is acidified and then recrystallized using hot ethanol to obtain it with high purity.

The azo polymerization with methylene di azo cyanate was prepared by weighing (0.25 g) of Azo1 and dissolving in (15ml) of chloroform. (1 g) of MDI was added to the solution and mixed well, then reflux and drip for half an hour. Afterward the prepared solution was put in a beaker for 24 hours. The solution is placed in an oven at 50°C for 3 hours, and then the temperature is raised to 100°C for 2 hours to complete the solidification process. The polyurethane was grafted on iron oxide (Fe₃O₄) nanoparticles prepared by the coprecipitation method [7, 8] to obtain the PU-MNPs as previously described [9].

Batch adsorption studies

To find the adsorption isotherm by preparing different concentrations of the Adsorbate within the range (of 100-300 mg/L) of Lead ion and Chromium ion and Cadmium ion (50 ml) was added in a series of solutions of heavy metals to (0.025g) from the prepared (PU-MNPs) adsorbents, and these solutions were placed in a shaker at a speed of (300) cycles/ minute for 24 hours and upon reaching the equilibrium time and after then separation and clear solutions were measured by atomic absorption spectroscopy and from knowing the values of absorption at the concentration at equilibrium, then finding the amount of the adsorbed substance from the below equation:

$$Q_e = (V_{sol} (C_0 - C_e)) / m$$

Where: For Primary Concentration: C₀ (L) Total volume of the adsorbent solution: V_{sol} (mg/g) Adsorbent for Final Concentration: C_e (mg/L) Adsorbent, (mg/g) Adsorbent Quantity: Q_e (g)

Adsorbent Weight: m.

RESULTS AND DISCUSSION

IR Spectrum of Azo compound, polyurethane, Iron oxide nanoparticles and Iron oxide nanoparticles –Polyurethane Characterization is shown in Fig. 1 and as described before in our previous work [9]. The effective aggregates of azo compounds, polymer and iron oxide nanocomposite are shown in Table 1 [10-12]. The Field Emission Scanning Electron Microscopy (FESEM) image of the Fe₃O₄ NPs is shown in Fig. 2 reflecting the size of synthesized nanoparticles [13].

Measurement of polymer decomposition by Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA and DSC)

In the case of DSC, many variables that can be observed on polymers can be known through measurement. For example, it is possible to know the melting point T_m, the degree of glass transition T_g, in addition to the possibility of

measuring the crystallization temperature and calculating the percentage of crystallization as well as calculating or knowing the solidification energy of hardened polymers thermally [14]. While in the case of TGA, the temperature can be known as the disintegration of polymers, as well as the remainder of them after the decomposition process, in addition to calculating the rate of disintegration as this information gives us a clear perception of the nature of those materials to know the possibility of using them in the right place.

Through the DSC curves shown in Fig. 3 that the behavior of PU is almost similar and both polymers did not suffer any significant change up to 500°C, but then two heat-emitting bands appeared at a temperature of 576,670 for PU and this is attributed to the dissolution of the polymers at these temperatures and their transformation into volatile gases while retaining some of the remaining ones according to their nature and this can be calculated through the [15] TGA technique. As for the TGA curves, through the curves shown

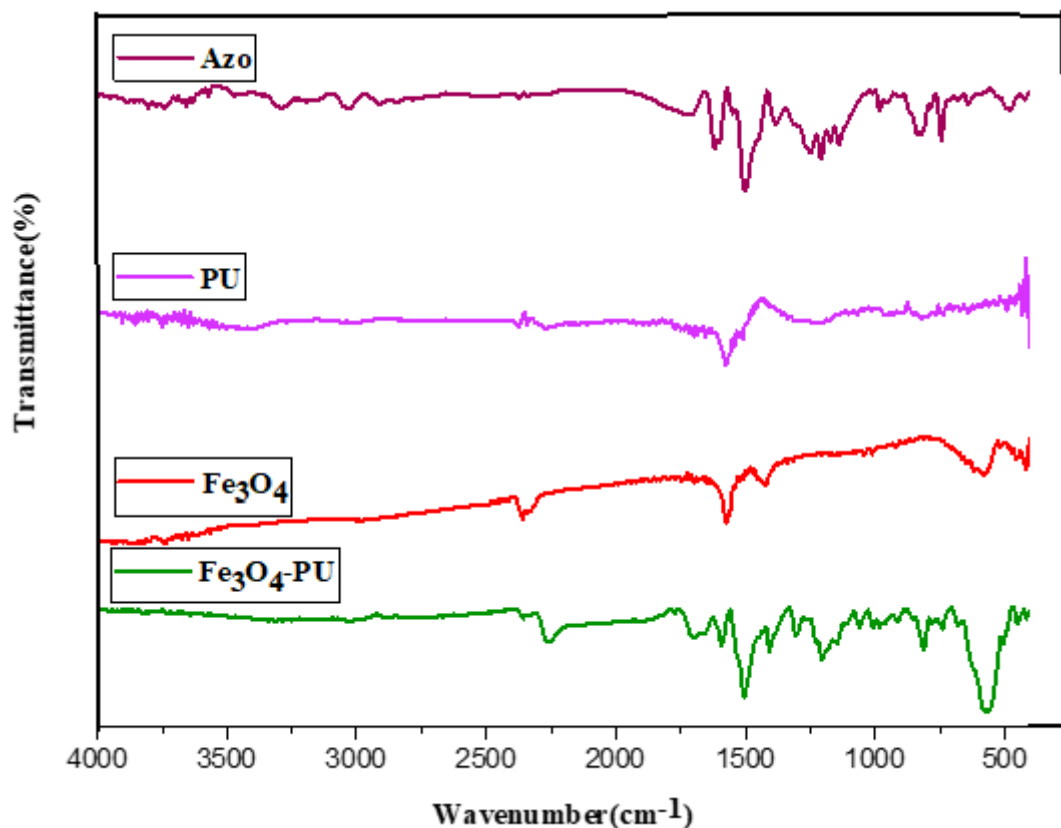


Fig. 1. Azo compound, polyurethane, Iron oxide nanoparticles and Iron oxide nanoparticles –Polyurethane

Table 1. Effective aggregates of azo compounds, polymer and iron oxide nanocomposite [12-14].

Wavenumber	Assignment groups
3452	O-H
3375	N-H
3028	C-H aromatic
2916	C-H (-CH ₂) Asymmetry
2843	C-H (-CH ₂) Symmetry
2276	(N=C=O) Isocyanate
1708	C=O stretching
1620	C=C aromatic stretching
1573	Fe=O
1537	(N=N) stretching azo
1300	C-H bending alkanes
1200	C- N stretching
1172	C- O -O
812	C=C bending out of plan
574,455	Fe-O stretching out of plane

in Fig. 2 we note that the PU polymer has one degree of dissociation above 200 ° C, as it was observed that the polymer PU disintegrates at a temperature of 252,511 degrees Celsius, on the other hand, it was observed that the remaining polymer at a temperature of 800 degrees Celsius is and 1% of the polymer PU, respectively, and this gives a clear perception that PU is heat-resistant. The differential Scanning Measurement (DSC) of polyurethane Compound is displayed in Fig. 4.

Adsorption of heavy metals ions

The adsorption of heavy metal ions, including cobalt and nickel ions, was studied on the modified PU-MNPs surfaces in this study, including nanomonium oxide coated with polyurethane at the best ratio (2:1). Magnetic iron oxide

nanoparticles MNPs in the Nano-polyurethane mixture have the characteristic of a large surface-to-volume ratio, and therefore have high surface energies. As a result, they tend to agglomerate to reduce their surface energies [16] Moreover, MNPs alone have high chemical activity and are easy to oxidize in the presence of oxygen (especially magnetite) leading to a loss of magnetism or dispersion, but if is bound to the polymer it leads to activity chemically balanced on the surface of the neutral polymer, resulting in increased magnetism and dispersion on the polymer surface. It is necessary to develop an active protection strategy to maintain the stability of these NPs through appropriate surfactant interaction as in the surface of the polymer used in this study [17, 18].

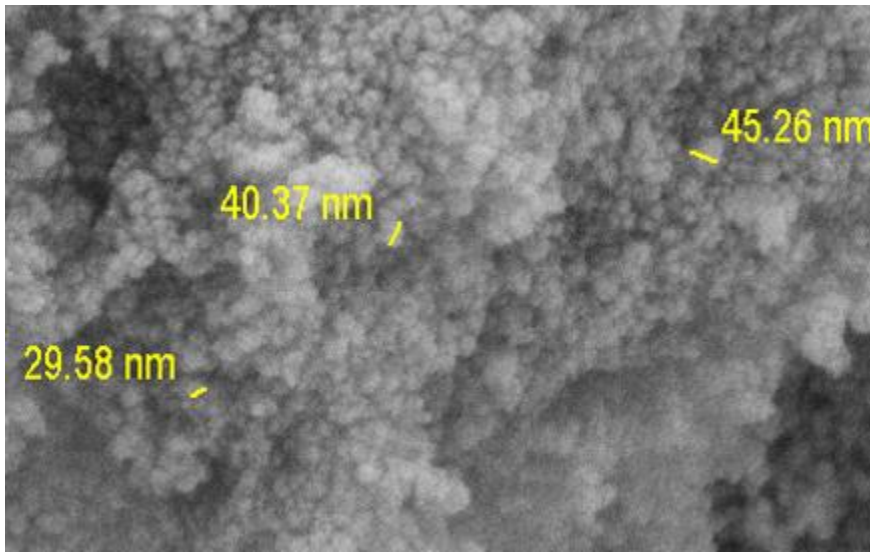


Fig. 2. FESEM images of the Fe₃O₄ NPs [15]

The surface charge of the MNPs can affect the agglomeration of nanomaterials and the absorption of ions on the Nano surface [19, 20]. To agglomerate over time in groups to form the basic structure, and produce electrostatic forces of attraction to deposit polyurethane on its surface due to the opposite charge of the polyurethane solution, while the produced PU- MNPs mixture is characterized by high stability and homogeneity due to the repulsive force between the particles indicated by the huge negative surface charge of

the particles By increasing the stability of (PU- MNPs) in plankton, the adsorption and removal of various pollutant particles on the surface of polyurethane will be improved [21, 22].

Effect of metal ions Concentration

Different Pb (II), Cr (III) and Cd (II) ions solutions were prepared; the initial concentrations were as follows 100, 150, 200, 250, and 300 in order to study the initial concentration effect at room temperature and optimum conditions obtained

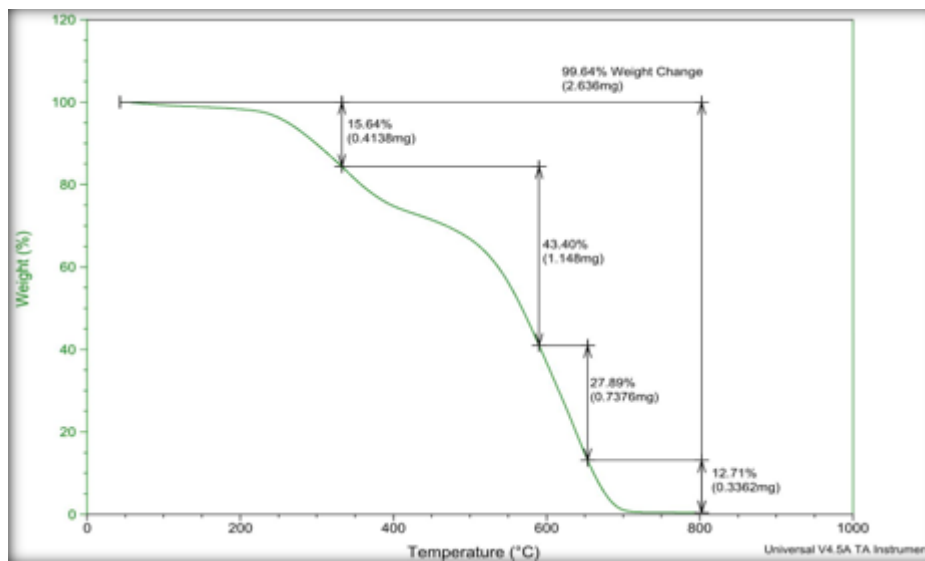


Fig. 3. Measurement of Thermogravimetric (TG) Decomposition of Polyurethane Compound

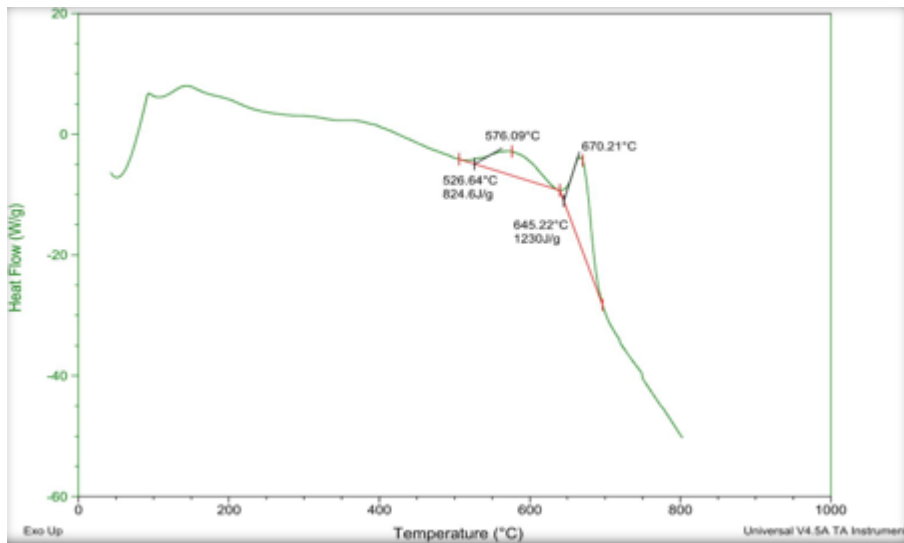


Fig. 4. Differential Scanning Measurement (DSC) of polyurethane Compound

previously to apply the Langmuir and Freundlich adsorption isotherms. The initial concentration of the adsorbent material increases, a decrease in the removal ratio and an increase in the adsorption capacity may be attributed to the increase in the rate of diffusion and mass transfer on the surface, and then the time required to reach the equilibrium state will be longer. A certain amount of the adsorbent increases with the increase in the initial concentration of the adsorbent at a constant

temperature [23].

Equilibrium time

To evaluate the time necessary for the adsorption process was conducted to calculate the adsorption time of the mixture (PU-MNPs) on the surface (Pb^{2+} , Cr^{3+} , Cd^{2+}) and the results showed that the equilibrium time for the lead was (60 min), for chromium was (30 min) and for cadmium (45 min), as shown in the Fig. 5.

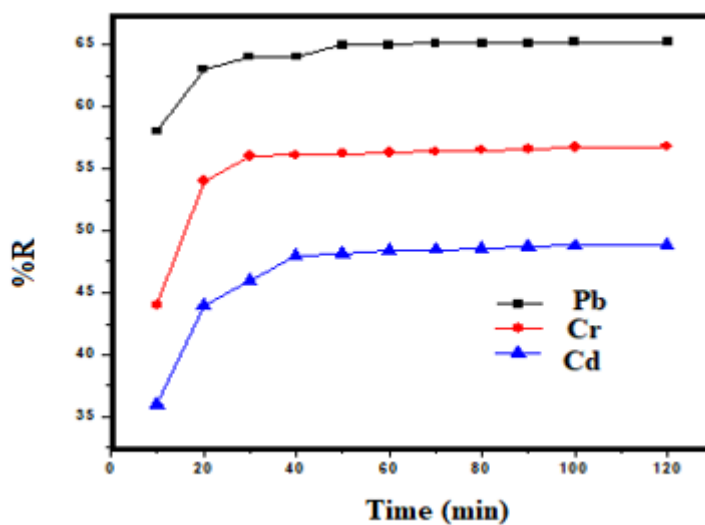


Fig. 5. Equilibrium time curve of Lead ion Pb (II), Chromium ion Cr (III), and Cadmium ion Cd (II) element on the surface of the mixture (PU-MNPs)

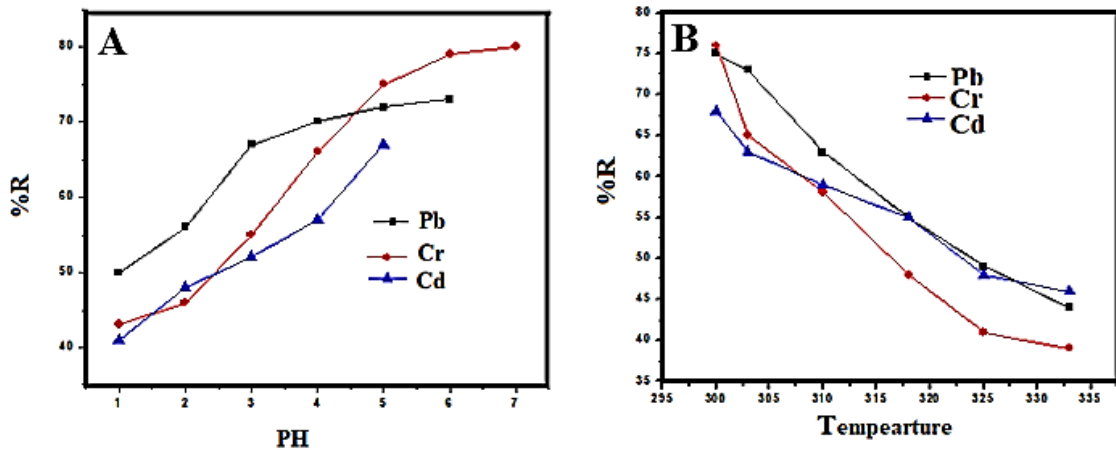


Fig. 6. (A) Effect of acidity function, (B) effect of temperature on Lead ion Pb (II), Chromium ion Cr (III), Cadmium ion Cd (II) adsorption on the surface of the mixture (PU-MNPs)

The removal percentage of Pb²⁺ increased with increasing the contact time, it tended to the equilibrium after 60 min, while Cr³⁺ tended to the equilibrium status after 30 min, while Cd²⁺ tended to the balance after 45 min. The rapid increase in the removal percentage at the beginning of the adsorption process was due to a large number of vacant adsorbent surfaces on the nanocomposite material (PU-MNPs). This is considered as a fast diffusion of metal ions in the adsorption material

[24].

Determination of pH

A study was conducted to study the effect of the acidity function of the adsorption process of heavy metal ions Pb²⁺, Cr³⁺ and Cd²⁺, on the fabricated PU-MNPs nanoparticle surfaces, where the removal percentage increases with the increasing of the amount of the acid function. The current results showed that the maximum adsorption for the lead

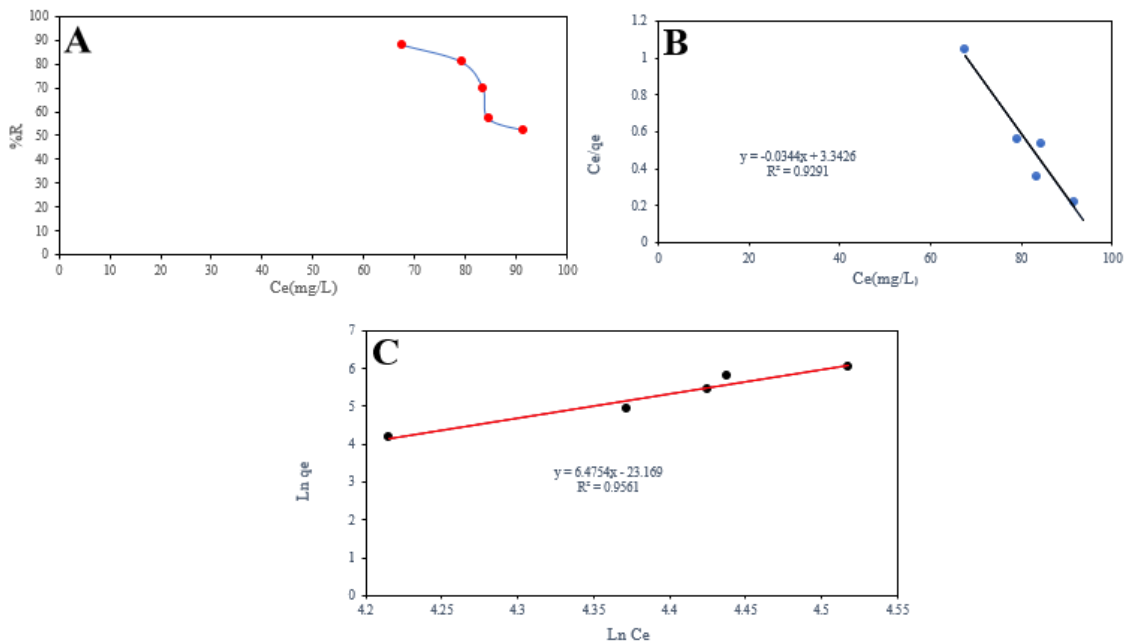


Fig. 7. (A) The percentage, (B) Lankemuir isotherm, (C) The Freundlich isotherm for adsorption of the Lead ion Pb (II) on the surface of the mixture (PU-MNPs) at a temperature of C°25, pH 6 and the initial concentration 250 mg/L

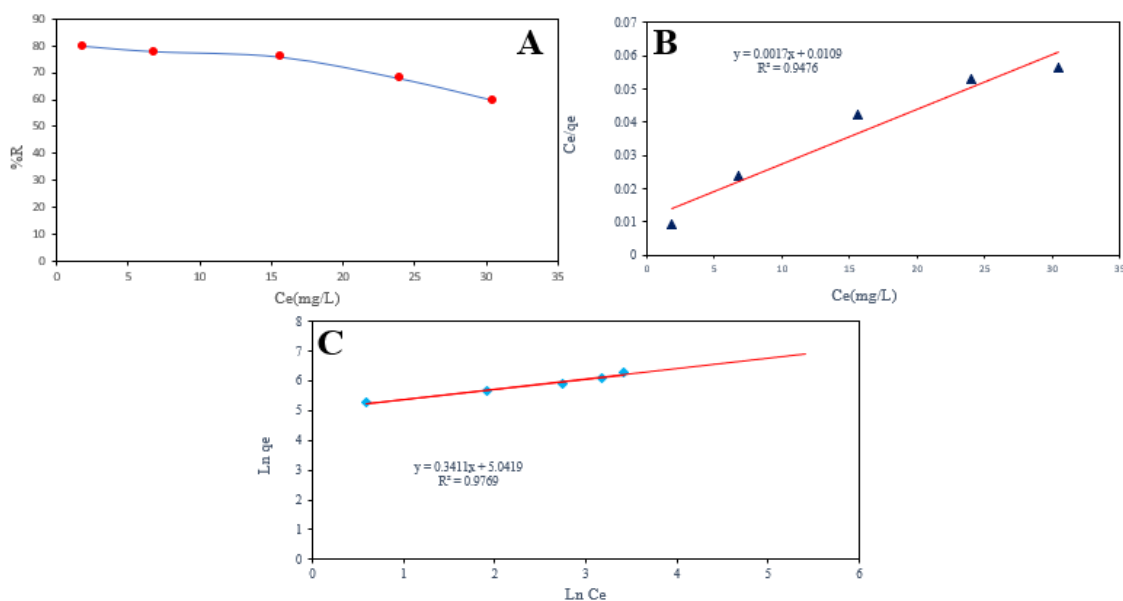


Fig. 8. (A) The percentage, (B) Langmuir isotherm, (C) The Freundlich isotherm for adsorption of the Chromium ion Cr (III) on the surface of the mixture (PU-MNPs) at a temperature of 25 °C, pH 6 and the initial concentration 250 mg/L

ions was at pH equal to 6, while for chromium ions was equal to 7 and for Cadmium ions was equal to 5. Since one end of the polymer has a negative charge, most of the ions are located in some reaction sites in the adsorbent material due to the presence of competing for positive ions in the solution being acidic and did not exceed the base pH values. This leads to a total reduction of the values of the adsorption sites affinity on the metal ion nanocomposite materials. This is due to the increase in the obstacles to the diffusion of metal ions caused by the positive repulsive forces of the increasing cation at moderate pH values [25]. The adsorbent material is relatively negatively charged more than the ionic solution, and this contributes to an increase in affinity for metal ions at pH values 5 [26], a higher pH (pH > 7) was not used in the current study to avoid removal of metal ions by precipitation [27] as shown in Fig. 6 A.

Effect of the Temperature

The degree of adsorption depends on the temperature of the liquid-solid interface. Adsorption studies were performed at different temperatures 300, 303, 310, 318, 325 and 333. The removal percentage of metal ions decreased with the increase in temperature. It was found that a lower temperature was better for the adsorption process. Thus, the process was concluded to be

exothermic and automatic [28]. The decrease in the adsorption capacity of nanocomposite materials with increasing temperature was due to the weak bonds carrying metal ions on the adsorbent surfaces of the nanocomposite. The increase in the temperature also degraded the regular structure of the nanocomposite materials, which leads to the loss of adsorption sites, thus reducing the removal efficiency of Cd(II), Cr(III), and Pb (II) ions. The decrease in the adsorption efficiency with increasing temperature indicated weak bonding interactions between the adsorbent surfaces and the cations; this is an indication that the process can be exothermic and thus leads to the conclusion that the adsorption process was appropriate at lower temperatures [29] as shown in Fig. 6 B.

Adsorption Isotherms

The percentage of adsorption of the Lead ion Pb (II) on the surface of the mixture (PU-MNPs) at a temperature of 25 °C, pH 6 and the initial concentration 250 mg/L is shown in Fig. 7A, while the Langmuir isotherm and the Freundlich isotherm for the same ion is presented in Fig. 7B and Fig. 7C respectively. The percentage of adsorption of the Chromium ion Cr (III) on the surface of the mixture (PU-MNPs) at a temperature of 25 °C, pH 6 and the initial concentration 250 mg/L

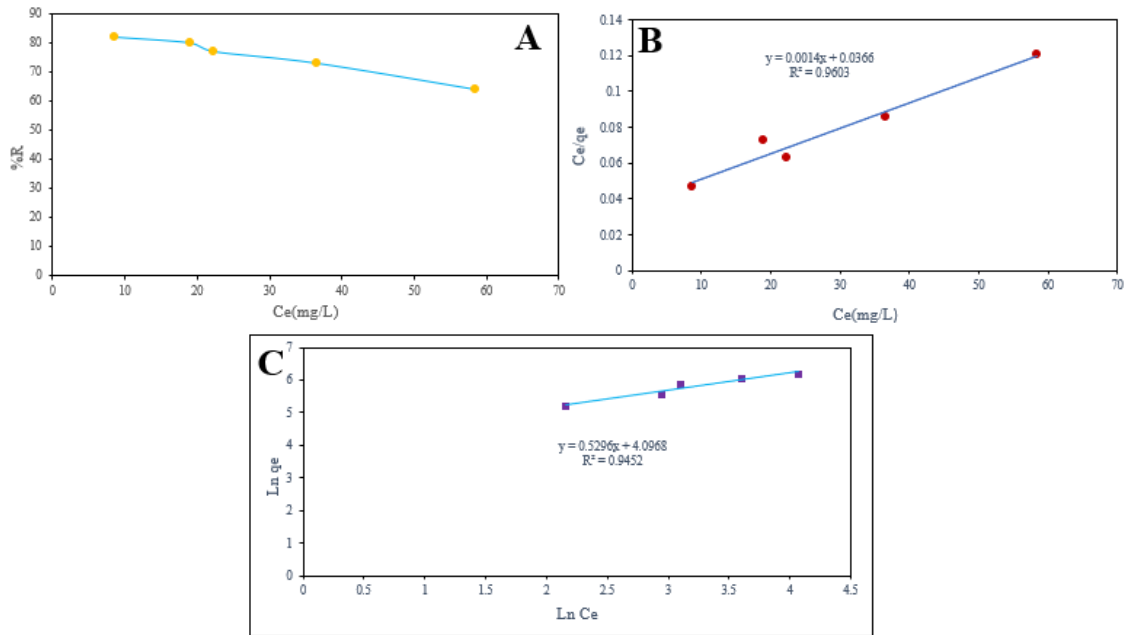


Fig. 9. (A) The percentage, (B) Lankemuir isotherm, (C) The Freundlich isotherm for adsorption of the Cadmium ion Cd (II) on the surface of the mixture (PU-MNPs) at a temperature of C°25, pH 6 and the initial concentration 250 mg/L

Lis shown in Fig. 8A, while the Lankemuir isotherm and the Freundlich isotherm for the same ion are presented in Fig. 8B and Fig. 8C respectively. While the percentage of adsorption of the Cadmium ion Cd (II) on the surface of the mixture (PU-MNPs) at a temperature of 25 °C, pH 6 and the initial concentration 250 mg/L is shown in Fig. 9A, while the Lankemuir isotherm and the Freundlich isotherm for the same ion are presented in Fig. 9B and Fig. 9C respectively.

Equilibrium uptake of Pb²⁺, Cr³⁺ and Cd²⁺ was investigated with sorption 0.025 g of Fe₃O₄-PU

in contact with 50 ml of solution at different PH points names 6, 7, 5 for Pb²⁺, Cr³⁺ and Cd²⁺ and the contact time was of different time slots at 60, 30, 45 min for Pb²⁺, Cr³⁺ and Cd²⁺ respectively at 25 °C temperature. The graphic between Ce versus Ce/Qe for the compatibility is greater for the Lankemuir model of the Cadmium ions, which agrees in both models. (7C), (8C), (9C), the graphic between Ln Ce versus Ln qe for the compatibility is greater for the Freundlich model for the Lead and Chromium ions, which is in agreement in both models. The Freundlich equation is used to describe

Table 2. Lankemuir and Freundlich constants for adsorption of Lead, Chromium, and Cadmium ions on the surface of the mixture (PU-MNPs).

Metal ion	Langmuir equation			Freundlich equation		
	K _L	Q max	R ²	K _F	1/n	R ²
Pb (II)	-0.01029	-29.0698	0.9291	2988134	0.0431	0.9561
Cr (III)	0.188889	588.2353	0.9476	2.19331	0.1983	0.9769
Cd (II)	0.038251	714.2857	0.9603	3.385322	0.244	0.9452

the adsorption characteristics of heterogeneous surfaces, as it considers the presence of effective sites and a heterogeneous adsorption surface and different energies and adsorption in several layers [30].

RL is indicative of the isotherm shape and predicts whether a sorption system is either favorable ($0 < R_2 < 1$), unfavorable ($R_2 > 1$) or irreversible ($R_2 = 0$). Figs. 7, 8, and 9 give the plots of the Langmuir and Freundlich isotherms of Pb²⁺, Cr³⁺ and Cd²⁺ ions adsorbed onto (PU-MNPs) respectively, and Table 2 displays Q_{max} , K_L , K_F , and the correlation coefficient R² results for the Langmuir and Freundlich isotherms for the adsorption of surface (PU-MNPs) by the Prepared adsorbents, The results showed that the adsorption follows the Langmuir and Freundlich equations. It was noticed that the Pb (II) lead ions follow the Langmuir and Freundlich isotherms, Great value R in the case of Freundlich isotherm which indicates that it is a physical adsorption,

As well as the Chromium ion, Cr (III) also follows the two equations, also great value R in the case of Freundlich isotherm, which indicates that it is a physical adsorption. The cadmium ion Cd (II) also follows the two equations Great value R in the case of Langmuir isotherm, which indicates that it is physical adsorption. Maximum adsorption of Cd (II) > Cr (III) > Pb (II) [31].

CONCLUSION

The adsorption of heavy metals (Pb²⁺, Cr³⁺ and Cd²⁺) using (PU-MNPs) surface has been determined. This study indicates that (PU-MNPs) have a good capacity for adsorption of the heavy metal ions. The percentage removal depended on pH, adsorbent concentration and adsorbent dosage. The maximum adsorption capacity was found at pH=6 for Pb²⁺, pH=7 for Cr³⁺ and at pH=5 for Cd²⁺, the adsorbent dosage was 0.025 g, and the initial concentration was 250 mg/L for Pb²⁺, Cr³⁺ and Cd²⁺. The best contact time was within 60, 30, and 45 min for Pb²⁺, Cr³⁺ and Cd²⁺ respectively. The adsorption process supplied Freundlich and Langmuir, isotherm models. This material can be successfully used as an environment-friendly product for the removal of heavy metals from the aqueous solutions.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this

manuscript.

REFERENCES

1. Benkhaya S, M'Rabet S, El Harfi A. Classifications, properties, recent synthesis and applications of azo dyes. *Heliyon*. 2020;6(1):e03271.
2. Carmen Z, Daniel S. Textile Organic Dyes – Characteristics, Polluting Effects and Separation/Elimination Procedures from Industrial Effluents – A Critical Overview. *Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update: InTech*; 2012.
3. Sharmin E, Zafar F. Polyurethane: An Introduction. *Polyurethane: InTech*; 2012.
4. Kadir NNA, Shahadat M, Ismail S. Formulation study for softening of hard water using surfactant modified bentonite adsorbent coating. *Applied Clay Science*. 2017;137:168-175.
5. Matlock MM, Howerton BS, Atwood DA. Chemical precipitation of heavy metals from acid mine drainage. *Water Research*. 2002;36(19):4757-4764.
6. Feng D, Aldrich C, Tan H. Treatment of acid mine water by use of heavy metal precipitation and ion exchange. *Minerals Engineering*. 2000;13(6):623-642.
7. Mohammadi T, Moheb A, Sadrzadeh M, Razmi A. Modeling of metal ion removal from wastewater by electrodialysis. *Separation and Purification Technology*. 2005;41(1):73-82.
8. Wang F, Yu X, Ge M, Wu S, Guan J, Tang J, et al. Facile self-assembly synthesis of γ -Fe₂O₃ /graphene oxide for enhanced photo-Fenton reaction. *Environmental Pollution*. 2019;248:229-237.
9. Khadim NS, Saleh HM, Abdulaali NA. Adsorption Capacity of Some Metal Ions Using Polyurethane Modified Magnetic Nanoparticles as Adsorbent. *Journal of Nanostructures*. 2022:1050-1062.
10. Rabab Yousry E, Prof. Magdy Mohamed A, Dr. Mohamed Ahmed Ibrahim A. Development of a Robust Hybrid Vehicle Power Management Control System. *International Journal of Engineering Research and*. 2015;V4(03).
11. Tombác E, Tóth IY, Nesztor D, Illés E, Hajdú A, Szekeres M, et al. Adsorption of organic acids on magnetite nanoparticles, pH-dependent colloidal stability and salt tolerance. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2013;435:91-96.
12. Kouli ME, Kourinou M, Kokkinopoulos I, Banis G, Savvidou M, Ferraro A, et al. Simple and rapid preparation of Fe₃O₄/β-cyclodextrin magnetic nanoparticles via microwave-assisted coprecipitation compared with a conventional method. *Journal of Biological Physics and Chemistry*. 2020;20(3):111-121.
13. Bagdatli E, Ocal N. Synthesis, Spectroscopic, and Dyeing Properties of New Azo and Bisazo Dyes Derived from 5-Pyrazolones. *Journal of Heterocyclic Chemistry*. 2012;49(5):1179-1186.
14. Synthesis, Characterization and dyeing performance studies of some azo dyes derived from m-phenylenediamine. *ZANCO Journal of Pure and Applied Sciences*. 2016;28(6).
15. Arifin' AMT, Supri AG, Hassan MF, Rahman MNA, Haq RHA, Taib I, et al. Effect of Filler Loading on Properties of Polyurethane/Clay Composites. *IOP Conference Series: Materials Science and Engineering*. 2019;607(1):012003.
16. Miztani E. Stochastic Interpretation for Whack-A-Mole Model. *Global Journal of Pure and Applied Mathematics*.

- 2017;13(11):7829.
17. Dhavale RP, Dhavale RP, Sahoo SC, Kollu P, Jadhav SU, Patil PS, et al. Chitosan coated magnetic nanoparticles as carriers of anticancer drug Telmisartan: pH-responsive controlled drug release and cytotoxicity studies. *Journal of Physics and Chemistry of Solids*. 2021;148:109749.
 18. Ghumman ASM, Nasef MM, Shamsuddin MR, Abbasi A. Evaluation of properties of sulfur-based polymers obtained by inverse vulcanization: Techniques and challenges. *Polymers and Polymer Composites*. 2020;29(8):1333-1352.
 19. Liu Y, Huang Y, Xiao A, Qiu H, Liu L. Preparation of Magnetic Fe₃O₄/MIL-88A Nanocomposite and Its Adsorption Properties for Bromophenol Blue Dye in Aqueous Solution. *Nanomaterials*. 2019;9(1):51.
 20. Maryamdokht Taimoory S, F. Trant J, Rahdar A, Aliahmad M, Sadeghfard F, Hashemzaei M. Importance of the Inter-Electrode Distance for the Electrochemical Synthesis of Magnetite Nanoparticles: Synthesis, Characterization, Computational Modelling, and Cytotoxicity. *e-Journal of Surface Science and Nanotechnology*. 2017;15(0):31-39.
 21. Kurnaz Yetim N, Kurşun Baysak F, Koç MM, Nartop D. Characterization of magnetic Fe₃O₄@SiO₂ nanoparticles with fluorescent properties for potential multipurpose imaging and theranostic applications. *Journal of Materials Science: Materials in Electronics*. 2020;31(20):18278-18288.
 22. Na Y, Yang S, Lee S. Evaluation of citrate-coated magnetic nanoparticles as draw solute for forward osmosis. *Desalination*. 2014;347:34-42.
 23. Wu W, He Q, Jiang C. Magnetic Iron Oxide Nanoparticles: Synthesis and Surface Functionalization Strategies. *Nanoscale Research Letters*. 2008;3(11).
 24. Mehdipour M, Ebrahimian Pirbazari A, Khayati G. Cobalt photodeposition on Fe₃O₄/TiO₂ as a novel magnetically separable visible-light-driven photocatalyst for efficient degradation of 2,4-dichlorophenol. *DESALINATION AND WATER TREATMENT*. 2019;155:329-340.
 25. Varenne F, Coty JB, Botton J, Legrand FX, Hillaireau H, Barratt G, et al. Evaluation of zeta potential of nanomaterials by electrophoretic light scattering: Fast field reversal versus Slow field reversal modes. *Talanta*. 2019;205:120062.
 26. Zhang L, Zeng Y, Cheng Z. Removal of heavy metal ions using chitosan and modified chitosan: A review. *Journal of Molecular Liquids*. 2016;214:175-191.
 27. Narayanan S. Kinetic and Equilibrium Adsorption Studies of Methylene Blue from Aqueous Solution Using Low-Cost Adsorbent. *International Journal of Psychosocial Rehabilitation*. 2019;23(4):1722-1738.
 28. Singh S, Ma L, Hendry M. Characterization of aqueous lead removal by phosphatic clay: Equilibrium and kinetic studies. *Journal of Hazardous Materials*. 2006;136(3):654-662.
 29. Mataka LM, Henry EMT, Masamba WRL, Sajidu SM. Lead remediation of contaminated water using Moringa Stenopetala and Moringa oleifera seed powder. *International Journal of Environmental Science & Technology*. 2006;3(2):131-139.
 30. McKay G. Adsorption of dyestuffs from aqueous solutions with activated carbon I: Equilibrium and batch contact-time studies. *Journal of Chemical Technology and Biotechnology*. 2007;32(7-12):759-772.
 31. Nejadshafiee V, Islami MR. Adsorption capacity of heavy metal ions using sultone-modified magnetic activated carbon as a bio-adsorbent. *Materials Science and Engineering: C*. 2019;101:42-52.