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RESEARCH PAPER

Heavy Metals Removal from Aqueous Solution Using (Cured Epoxy resin- lignin) Nanomagnetic Interpenetrating Polymer Network

Sajid Hassan Guzar [1], Samia Mezhr Merdas [2], and Salah Sh. Al-luaibi [3]*

[1] *Department of Chemistry, College of Education for Pure Sciences, University of Kerbala, Iraq*

[2] *Department of Chemistry, College of Science, University of Thi-Qar, Iraq*

[3] *Department of Chemistry, College of Science, University of Basra, Iraq*

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ABSTRACT

[(Cured epoxy resin- lignin) nanomagnetic interpenetrating polymer network (IPN)] (NM - IPN's) derived from cured epoxy with amine hardener and Lignin was synthesized by sequential polymerization in the presence of Fe_3O_4 nanomagnetic particles. The chemical structure and surface morphology of NM semi IPNS resin nanoparticles were characterized by Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). The thermal properties of (NM semi IPNS) have been evaluated by Thermogravimetric analysis (TGA) and Differential Scanning Calorimetric (DSC). Adsorption of Cu^{+2}, Pb^{+2}, Co^{+2} and Cd^{+2} was investigated under different conditions such as pH and time using flameless atomic absorption spectroscopy. The adsorption studies were evaluated by using Langmuir and Freundlich isotherms.

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INTRODUCTION

Heavy metals are used in many industries for different purposes and released to the environment with industrial wastage. Therefore, the effluents being generated by these industries are rich in heavy metals. Cadmium, zinc, copper, nickel, lead, mercury, arsenic, and chromium are such toxic metals, which are widely used and are often detected in industrial wastewaters, which in turn originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture dental operation, electroplating, textile, paper and pulp industry, printing and photographic industries, etc. [1]. Unlike organic wastes, heavy metals are non-biodegradable and can be accumulated in living tissues, causing various diseases and disorders, and are potentially toxic to humans [2]. Wastewaters are produced in large volumes, leading to an increase in the complexity of toxic effluents, therefore, they must be removed before discharge. Considering the aforementioned problems, it is a necessity to develop easily available, inexpensive, and equally effective alternatives for wastewater treatment. Several technologies have been developed over the years to remove toxic metals from wastewater. Many

* *Corresponding Author Email: Sajid.h@uokerbala.edu.iq*

researchers prepared superabsorbent hydrogels or copolymers based on natural and synthetic polymers to use them in the removal of metal ions in the semi-interpenetrating polymer network (s-IPN). IPN composites show excellent thermal stability and mechanical properties compared to those of single components [3-7]. In the last few decades, nanoparticles and nanocomposites have received a great deal of attention from scientists, due to their small sizes and related unique properties [4,5]. Nanocomposite materials formed by metal nanoparticles that were appropriately incorporated into the polymer matrix were found to be very significant due to their diversity in electrical, catalytic and optical properties. These diversities have potential applications in the fields of electronic, photonic, catalysis and bioengineering [8] Magnetite (Fe_3O_4) combined with polymers/nanocomposites has unique multifunctional properties for materials, such as small sizes, biocompatibility, low toxicity, and superparamagneticity, which is applied in medical fields and magnetic recording media [9-15]. Therefore, magnetite plays a potential key role in providing the desired electrical and magnetic properties in the final composite. This article focuses on polymeric nanocomposite employing nanomagnetic interpenetrating polymer networks derived from epoxy resin and lignin in the presence of nanomagnetic Fe_3O_4 to remove heavy metals such as Cu^{+2}, $Pb^{+2,}$ Co^{+2} and Cd^{+2} from wastewater.

MATERIALS AND METHODS

Materials

Thiourea, formaldehyde (37%), Epoxy , triethylenetetramine ,Iron (II) Chloride Hexahydrate ($FeCl_3.6H_2O$), Iron(III) Chloride Tetrahydrate ($FeCl_2.4H_2O$), Hydrochloric acid (HCl), Ammonium solution (NH_4OH), Lead (II) Nitrate ($Pb(NO_3)_2$), Copper(II) Nitrate($Cu(NO_3)_2$) and Cadmium (II) Nitrate (($Cd(NO_3)_2$) were used from Fluka /Switzerland .

Instruments

Thermal analysis was carried out using Thermal Gravimetric Analysis (TGA) (Perkin Elmer-TGA-4000), in the College of Science, University of Muthanna, at a heating rate of 20 °C /min in the temperature range (40-605 °C) under Nitrogen atmosphere with a flow rate of 20ml/min and Differential Scanning Calorimetric (DSC) analysis in the College of Engineering, University of Tehran, at the heating rate 10 °C /min in the temperature range (0-600 °C) under nitrogen atmosphere. The Fourier Transform Infrared (FT-IR) spectra of the samples were recorded by (Shimadzu, Japan) in the Department of Chemistry, College of Science, University of Thi-Qar by KBr disks, at ambient temperature. The morphology of the surface was examined by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) in the College of Engineering, University of Tehran.

Nanomagnetic IPNs

The [(epoxy resin - Lignin) nanomagnetic IPNs] (NM – IPN's) were prepared by mixing nanomagnetic particles (Fe_3O_4) and epoxy resin ((1:0.5)) and Lignin with a weight ratio of (0.1:1:.01). Then the temperature was increased up to 50 °C with stirring for 90 min to initiate nanomagnetic IPNs polymerization. The product was poured into a glass mold and kept in the oven at 70 °C for 24 hrs. Then post cured 3hrs at 100°C.

Adsorption Experiments

The adsorption studies were carried out at 25 °C. The pH of the solution was adjusted to different values according to the requirements, with different concentrations of hydrochloric acid (HCl) and ammonia solution. Known amounts of different adsorbents were added to (Co^{+2}, Cu^{+2}, Cd^{+2}, Pb^{+2}) samples separately and allowed sufficient time for adsorption equilibrium. The effects of various parameters on the rate of adsorption process were investigated by varying contact time, (10, 20, 30, 1, 2, 24) hr, adsorbent amount (0.05g), initial pH of the solution (2,4,6,8), agitation speed (180 rpm) and temperature (25 °C). The solution volume was kept constant at 10 ml. After attaining the adsorption equilibrium, all these mixtures were filtered. Filtrates were analyzed for (Cu^{+2}, Cd^{+2}, Pb^{+2}) by flame atomic absorption spectrophotometer working at resonance wavelengths (324.75, 228.8, 283.31) nm, respectively. The equilibrium adsorption capacity, q_e (mg /g) and the percentage removal of metal was calculated using the mass balance, according to the following equation [15-18]:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where V is the sample volume (L), m is the mass of the adsorbents (g), C_o is the initial metal ion concentration (mg/L), and C_e is the equilibrium

concentration of a metal ion in the solution (mg/L). The concentration of metal ions in the solution was determined using Atomic Absorption Spectrometer.

Study of adsorption isotherms

10 ml of five solutions with concentrations 1, 10, 20, and 30 ppm were prepared by proper dilution of stock solution of (Co^{+2}, Cu^{+2}, Cd^{+2}, pb^{+2}). The optimum conditions of pH, adsorbent dose, adsorbent particle size, agitation speed, temperature and contact time were adopted according to the sample of adsorbent used for studying adsorption isotherm. In the end, suspensions were filtered off and the filtrates were analyzed for remaining (Co^{+2}, Cu^{+2}, Cd^{+2}, Pb^{+2}) concentration by using a flame atomic absorption spectrophotometer. Langmuir isotherm was plotted by using its standard straight-line equation (2):

$$\frac{1}{q} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \quad (2)$$

Where 'q' (mg g^{-1}) is the amount of metal ions adsorbed, 'C_e'(ppm) is the concentration of metal at equilibrium, q_m (mg g^{-1}) and b (L g^{-1}) are Langmuir isotherm parameters which were calculated from the slope and intercept values of the linear plot of 1/q versus 1/ C_e.

Freundlich isotherm was plotted using the following standard straight-line equation (3). The value of K_F can be determined from intercept and 1/n can be determined from the slope of the linear plot of log q versus log C_e. K_F and 1/n are Freundlich isotherm parameters.

$$\log q = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

RESULTS AND DISCUSSIONS

Characterization

FTIR spectroscopy

FTIR spectrum of nanomagnetic IPN's-IV (epoxy resin- lignin) nanomagnetic IPN's] (NM – IPN's) is presented in Fig. 1. The spectrum shows all the peaks corresponding to lignin and epoxy/hardener. A strong absorbance at 3448 cm^{-1} assigned to (–OH) stretching vibrations which correspond to the aromatic and aliphatic hydroxyl groups founded in lignin and epoxy. In addition, absorption bands at 2993, 2947 and 2846 cm^{-1}, assigned to stretching vibration of the aliphatic CH_2 group. Absorption bands for the carbonyl group were found at 1728 cm^{-1}. Also, the absorption band of aromatic C-H vibration was found at range (1400- 1612) cm^{-1} [19-21], while the peak at 540 cm^{-1} corresponds to Fe-O stretching modes [22-26].

Thermal Studies

Thermogravimetric Analysis (TGA) and derivative thermal gravimetric (DTG)

The thermal stability of nanomagnetic IPN's-IV Fig. 2 showed that two decomposition process stages were occurred. The first stage can be related

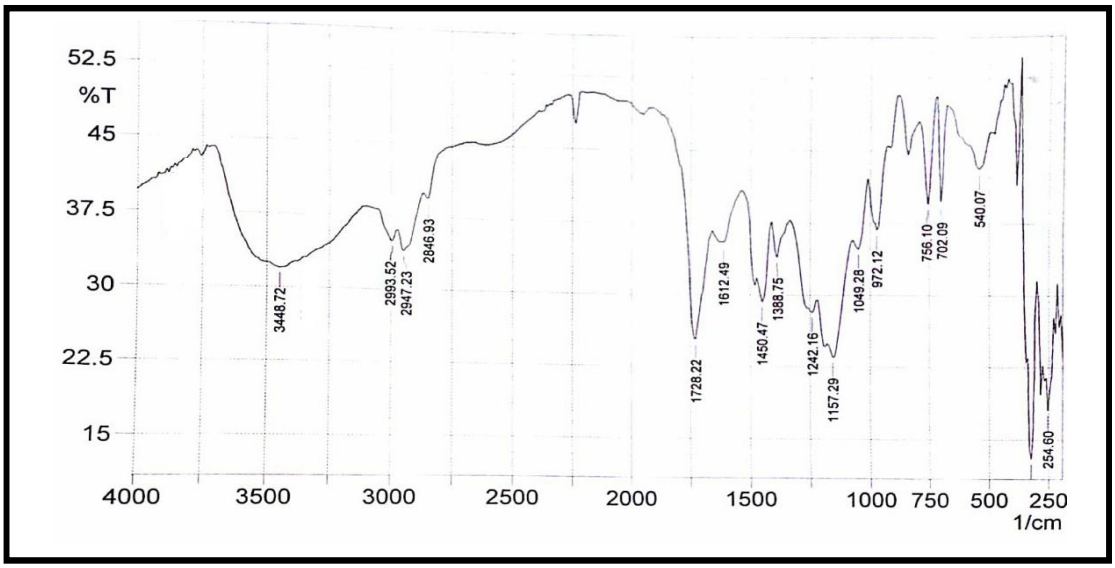

Fig. 1. IR spectrum of (NM – IPN's)

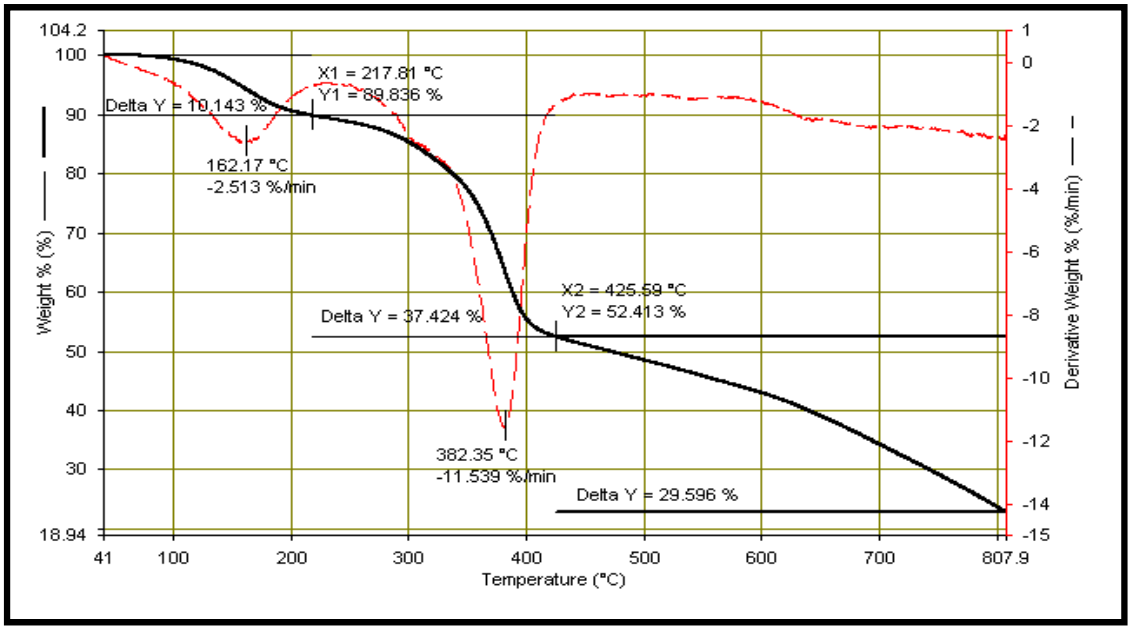

Fig. 2. TGA curve of (NM – IPN's)

to the evaporation of solvent (water) and low molecular weight resin, whereas the second stage is the main decomposition process with 37.4% lignin decomposing very slowly (< 0.15 wt%/°C), losing only 40 wt% of its initial mass below 700 °C. The degradation rate slightly increases 30 to 0.3 wt%/°C above 750 °C, the mass loss at 850 °C being of ~67 wt%. Thermal degradation of lignin is generally influenced by heat and mass transfer processes, which significantly affect the activate ion energy of the process and the pre-exponential factor.

Differential Scanning Calorimetric (DSC) analysis

The DSC thermograms of cured prepared nanomagnetic IPN's shown in Fig. 3 and showed that the endothermic peak was most likely due to the vaporization of water. This was in agreement

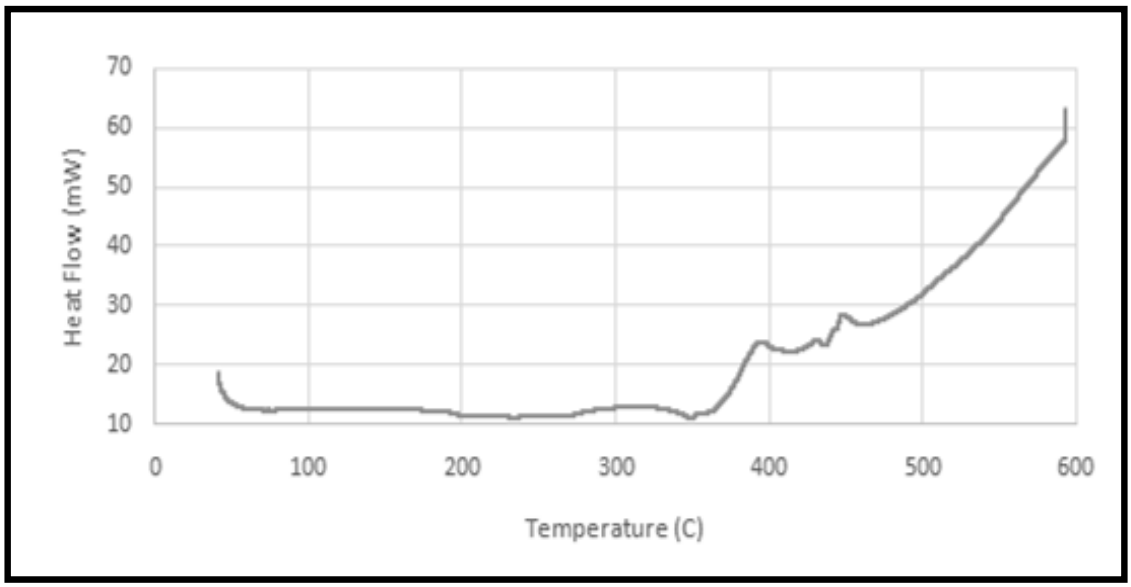

Fig. 3. DSC curve of (NM – IPN's)

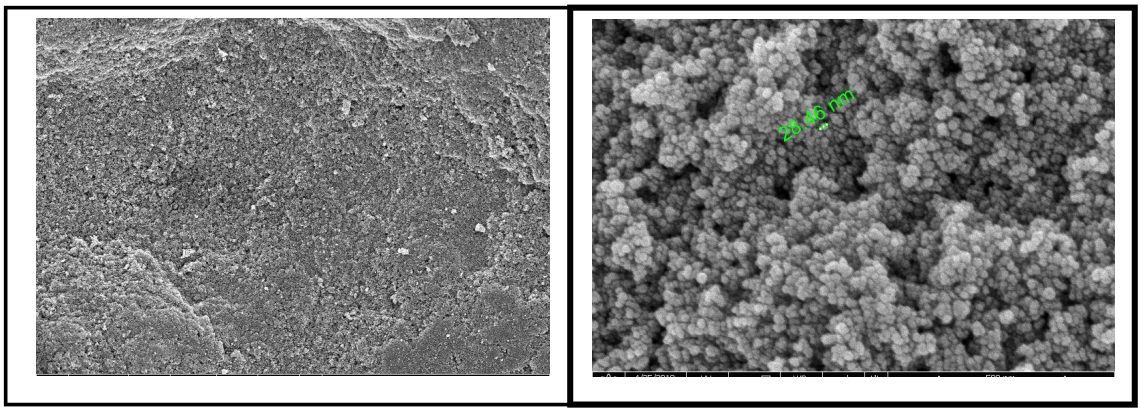

Fig. 4. SEM image of (NM – IPN's)

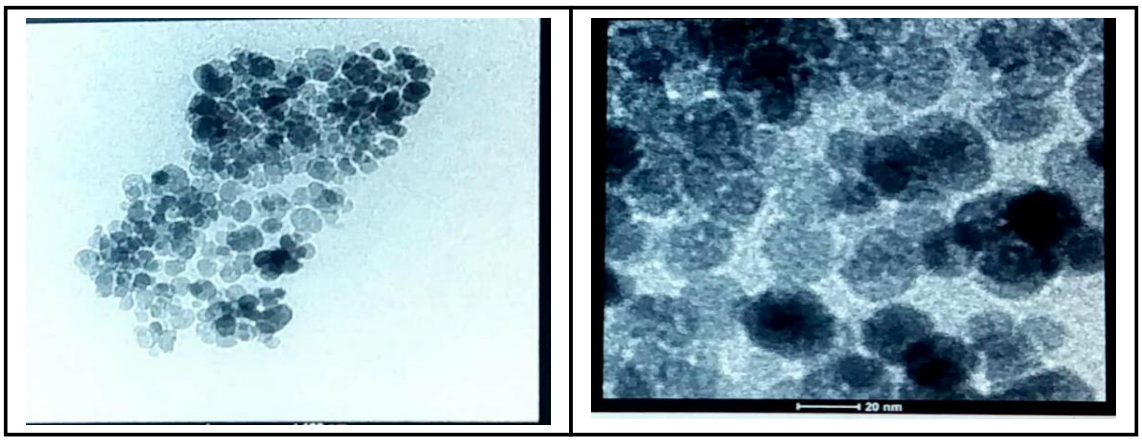

Fig. 5. TEM image of (NM semi IPN's)

with the TGA results and the degradation process has been very clear as exothermic peak in DSC thermograms for IPN's so no Tg and Tm were found in DSC thermograms.

Surface morphology

Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM)

The size and morphology structure of (NM -IPNs) were studied by Scanning Electronic Microscopy (SEM) and Transmission Electron Microscopy (TEM). Fig. 4 illustrates the spherical shape of the particles which are aggregated homogenously which is observed for IPNs components. This indicated that the magnetic particles are coated by IPNs components as a core-shell structure with a dark core of (Fe_3O_4) magnetic particles and a gray shell for linear polymers and network in nanomagnetic IPNs, which are in good agreement with the TEM results presented in Fig. 5.

Analytical study

The effect of pH on removal metal ions

The pH value of the aqueous solution is an important controlling parameter in the adsorption process. These pH values influence the surface charge of the adsorbent during adsorption. In order to assess the influence of this parameter on the adsorption, the experiments were carried out at different pH (2,4,6 and 8). The experiment was performed for (NM – IPN's) studies with an initial concentration of 0.05 g at room temperature with different contact times for solutions from Co^{+2}, Cu^{+2}, Cd^{+2}, and pd^{+2} ions. The effect of pH on the adsorption capacity followed a similar trend Fig. 6. At low pH values, the polymers exhibited a low adsorption capacity. This might be caused by two reasons, the competitive adsorption existed between the positively where there was an excess of H^+ ions in solution, a charged H^+ ions and the metal ions for the same active adsorptive sites,

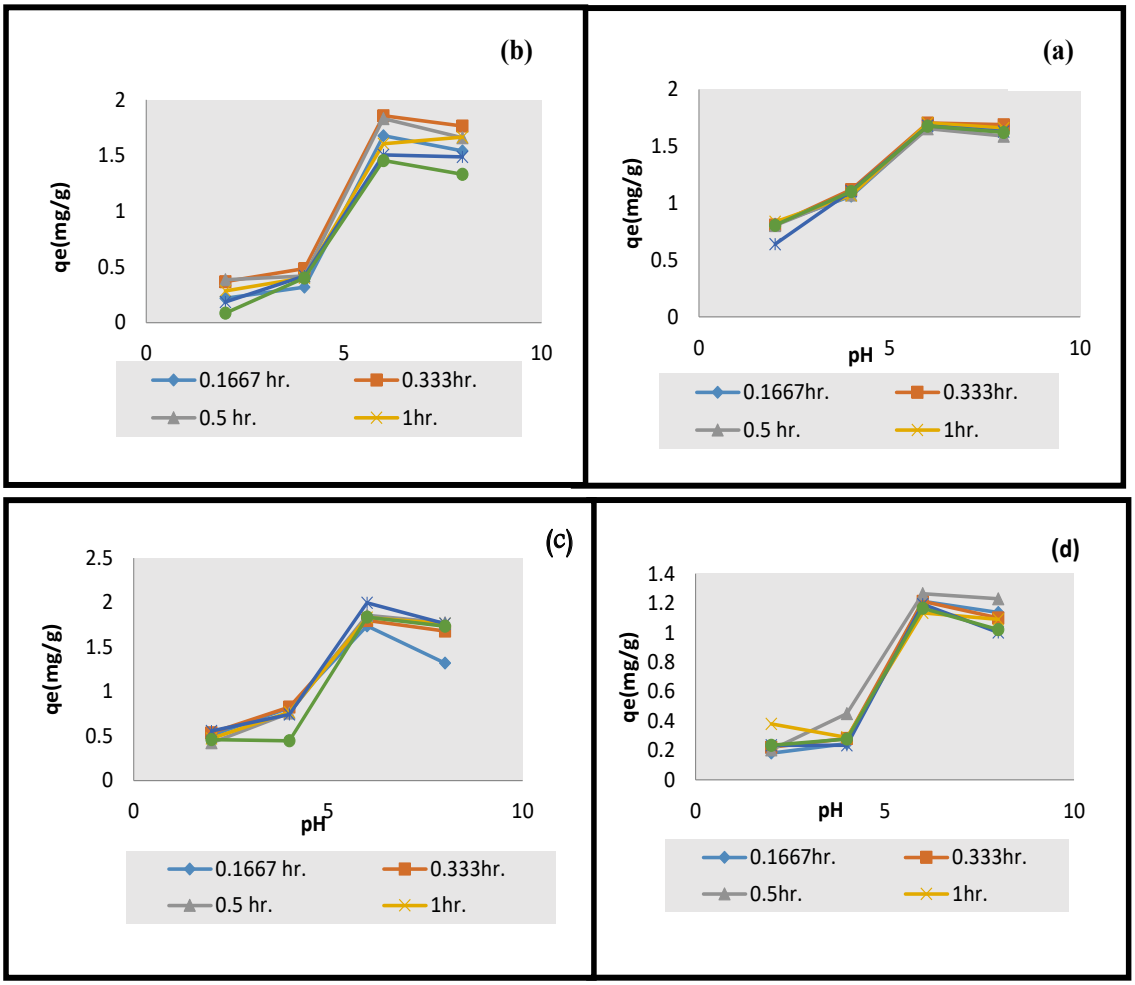

Fig. 6. Effect of pH on metals removal by (NM semi IPNs) : (a) pb^{+2} (b) Cd^{+2} (c)Cu^{+2} (d) Co^{+2}

which would result in the suppression of the metal ions adsorption onto the composite. On the other hand, at low pH values, the functions of polymers on the surface were protonated, which would cause a cationic repulsion between the metal ions and the active sites that were protonated. As the pH increased, the composite surface became less positive due to the decrease of proton competitive adsorption and therefore ionic exchange and electrostatic attraction between the metal ions and the polymer were likely to be increased and pH above 6 maybe the metal ions are precipitate

Table 1. Parameters of Freundlich and Langmuir constants for Adsorption

Freundlich Isotherm Parameters	Pb^{+2}	Cd^{+2}	Cu^{+2}	Co^{+2}
1/n	1.39	1.48	1.307	1.36
K_F	0.426	0.435	0.354	0.394
R^2_F	0.973	0.812	0.959	0.889
Langmuir Isotherm Parameters	Pb^{+2}	Cd^{+2}	Cu^{+2}	Co^{+2}
Qm (mg g^{-1})	1.077	0.312	0.902	0.504
b (L g^{-1})	0.096	0.178	0.079	0.124
R^2_L	0.997	0.911	0.993	0.997

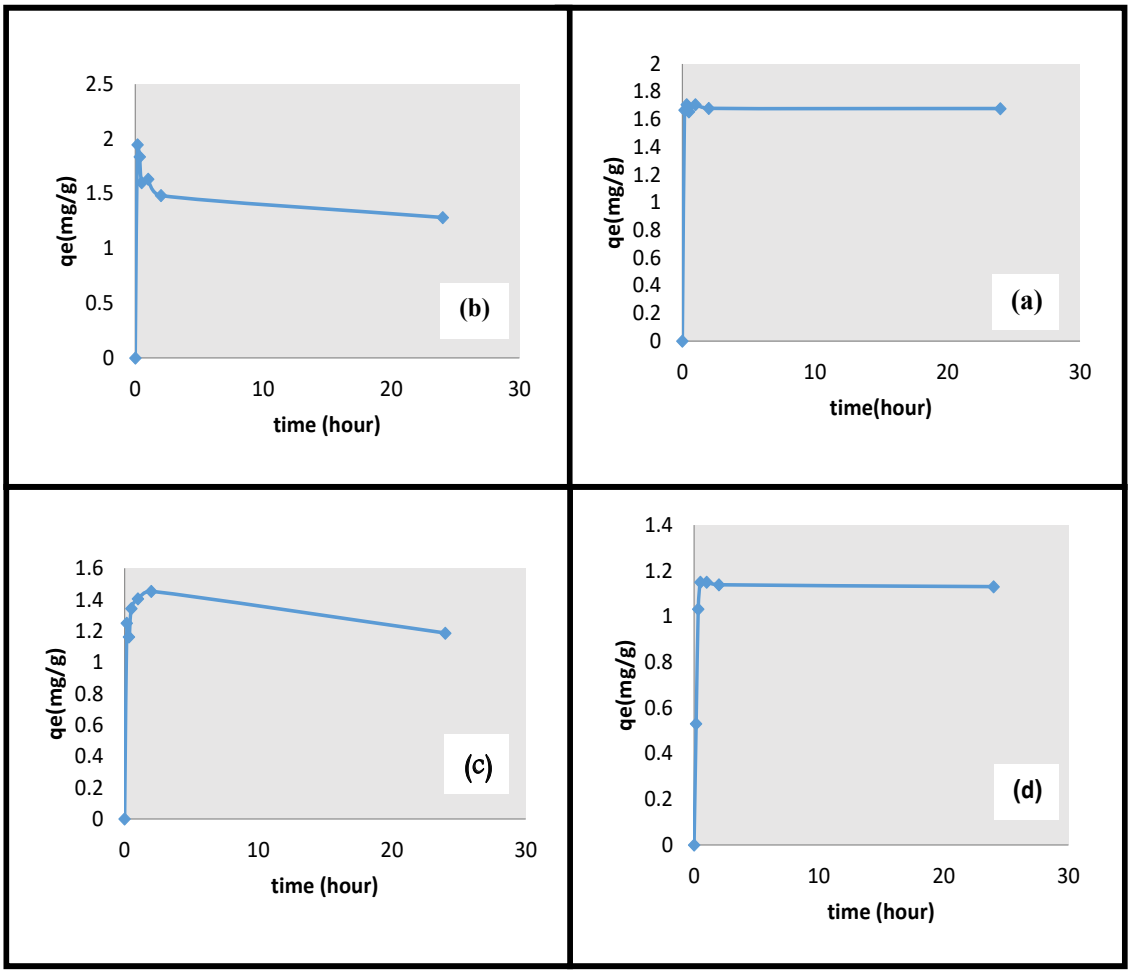

Fig. 7. Effect of contact time on metals removal by (NM semi IPN's) at pH=6: (a) pb^{+2} (b) Cd^{+2} (c)Cu^{+2} (d) Co^{+2}

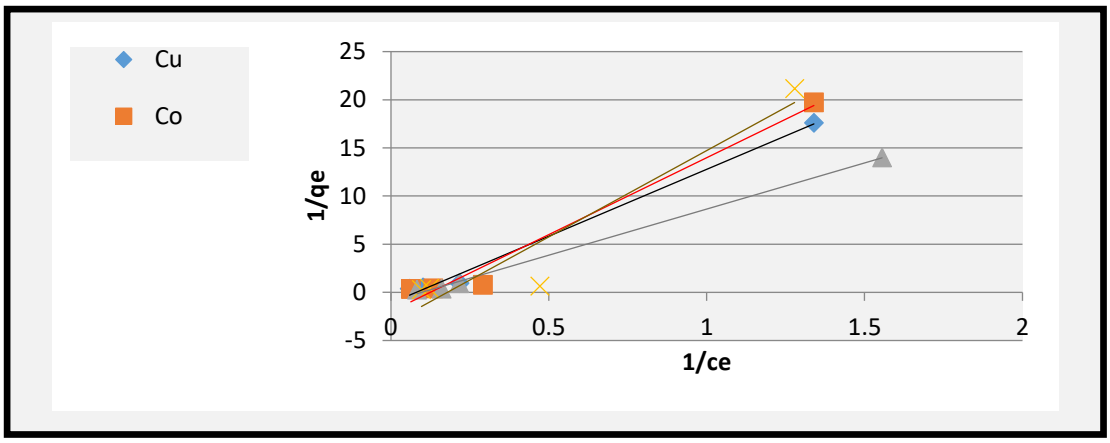

Fig. 8. Langmuir adsorption isotherm for metals adsorption by (NM semi IPN's) at pH=6, shaking rate 180 rmp, amount of adsorbent 0.05g)

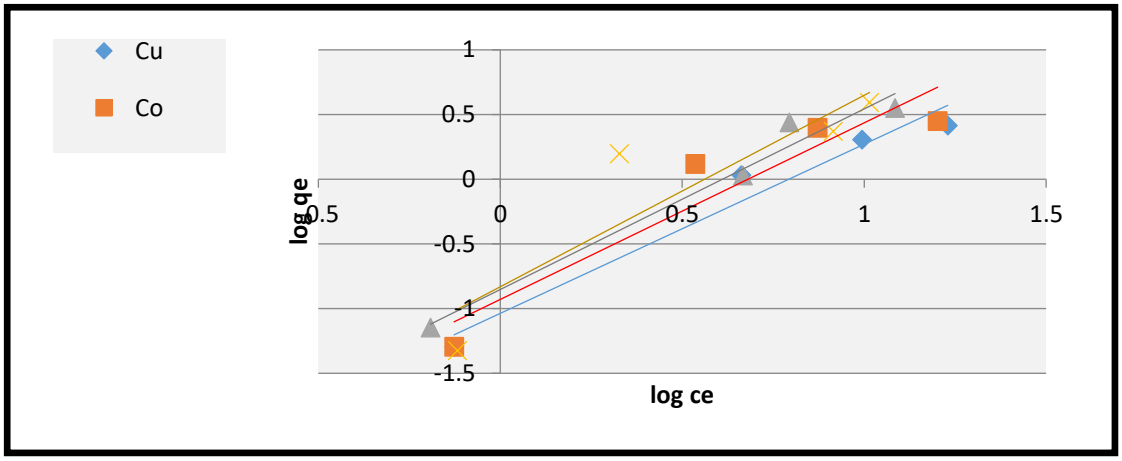

Fig. 9. Freundlich adsorption isotherm for metals adsorption by (NM semi IPN's) pH=6, shaking rate 180 rmp, amount of adsorbent 0.05g)

Table 2. Comparison of maximum adsorption capacity of (NM semi IPN's) with some other adsorbents

Adsorbent	Heavy metal	Qmax (mg g-1)	Source
Magnetite nanoparticles	Pb(II)	0.189	39
Sugarbeet pulp	Cu(II)	0.15	40
polyaniline/polypyrrole nanoparticles	Cd(II)	0.261	41
chromium doped nickel nano metal oxide	Cd(II)	0.1119	68

to form metal hydroxide.

Effect of time

The equilibrium adsorption capacity of Co^{+2}, Cu^{+2}, Cd^{+2} and Pb^{+2} on the surface of (NM – IPN's) as a function of contact time are shown in Fig.7. The adsorption rate is rapid in the beginning due to more active sites available on polymer, however, it gradually decreases until an equilibrium state is reached due to occupancy of active sites of adsorbent [27-29].

Adsorption isotherms

The adsorption studies were conducted by varying the initial metal ion concentrations (1,10, 20 and 30 ppm) with a constant dosage of adsorbent (0.05 g), at optimum pH=6 and optimum shaking time for capacity adsorption of all metal in this study. The Langmuir and Freundlich isotherms were shown graphically in Figs. 8,9 and the corresponding parameters were listed in Table 1. According to the coefficients of correlation obtained from linear regression, it was found that in all cases the Langmuir model fits the data better than the Freundlich model because the correlation coefficients (R_2) values are higher for Langmuir isotherm than for the Freundlich isotherm. This reinforces the fact that Langmuir isotherm is useful to explain the adsorption of all metals ions (Co^{+2}, Cu^{+2}, Cd^{+2}, Pb^{+2}) from the solutions on the surface (NM - IPNs) are prepared in this study when it follows the monolayer mode rather than the multilayer mode. A basic assumption of the Langmuir theory is that the sorption can take place at specific homogeneous sites on the adsorption. When a site is occupied by an adsorbate, no further adsorption can take place at that site.

CONCLUSION

The results of this study indicate that (NM -IPN's) can be successfully utilized for removal of Cd(II), Cu(II), Co(II) and Pb(II) from aqueous solutions. The adsorption of these metals was tested at different conditions such as contact time and initial pH. The optimum solution pH for

absorbing Cd(II), Cu(II) Co(II), and Pb(II) from an aqueous solution was found to be 6. The sorption of Cd(II), Cu(II) Co(II) and Pb(II) by (NM -IPN's) followed a monolayer sorption model Langmuir.

CONFLICT OF INTEREST

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

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