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[Poly(Thiourea-Formaldehyde) - Epoxy resin)] Nanomagnetic Full -IPN's for Removal of Heavy Metals from Aqueous Solution : Synthesis and Characterization

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Abstract:
In this work, a batch adsorption study was conducted to investigate the removal efficiency of lead (II), Copper (II) and Cadmium (II) from aqueous solutions by (poly (thiourea-Formaldehyde-Epoxy resin) nanomagnetic Full-IPN's (NM Full-IPN's). The NM Full-IPN's was synthesized by sequential polymerization with presence Fe_3O_4 nanoparticles. The chemical structure and surface morphology of NM Full-IPNS resin nanoparticles were characterized by Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). The chemical structure and surface morphology of NM Full-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 Full- IPN's) has been evaluated by Thermogravimetric analysis (TGA) and Differential Scanning Calorimetric (DSC). Adsorption of Pb (II), Cu(lI) and Cd(II) onto NM Full- IPN's agreed well with the Langmuir model, as revealed by the higher values of correlation coefficients. The results indicate that NM Full- IPN's could be used as efficient adsorbent for the removal of Pb (II), Cu(lI) and Cd(II) from aqueous solution

Keywords: Magnetic nanoparticles, Polymer nanocomposites, Heavy Metals, Adsorption Studies.

1. 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 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, disorders and are potentially toxic to humans (2). These waste waters are produced in large volumes. This leads to an increase in the complexity of toxic effluents, Therefore, they must be removed before discharge. However, problems with the aforementioned solutions make it necessary to develop easily available, inexpensive, and equally effective alternatives for waste water treatment (3,4,5). Number of technologies have been developed over the years to remove toxic metals from wastewater such as using maghemite, magnetite (Fe_3O_4), diatomite supported/unsupported magnetite nanoparticles, surface-modified jecobosite nanoparticles and Magnetic polymer nanocomposites [6-9]. During the last decade, Nanocomposites and magnetic nanoparticles have attracted considerable scientific and technological interest because of their applications in environmental remediation. The adsorbing power of inorganic magnetic nanomaterials is poor, but their incorporation into organic polymers and biomolecules can enhance the adsorption capacity. Moreover, the stronger ionic interaction between metal ions and composite surface occurs through pore diffusion that primarily enhances sorption–desorption dynamics. The separation is further facilitated due to magnetic core. The magnetic nanocomposite based on organic polymers and biopolymers thus offers a better alternative for conventional metal removal techniques because of ease of separation and administration [10]. This article focused about using of nanomagnetic particles (Fe_3O_4) coated with magnetic polymeric nanocomposite derived from epoxy resin and poly thiourea- formaldehyde to remove heavy metals such Cu^{2+}, Cd^{+2} and Pb^{2+} from waste water

2.Experimental:

2.1 Materials:

Thiourea, formaldehyde (37%), epoxy resin, triethylenetetramine, Iron (III) Chloride Hexahydrate ($FeCl_3.6H_2O$), Iron(II) Chloride Tetrahydrate (FeCl2.4H2O), Hydrochloric acid (HCl), Ammonium solution (NH4OH) were used from BDH/England, Lead (II) Nitratetetrahydrate ($Pb(NO_3)_2$), Copper(II) Nitrate($Cu(NO_3)_2$), Cadmium (II) Nitrate (($Cd(NO_3)_2$) were used from Fluka /Switzerland.

2.2. Instruments

Thermal analysis was carried out using thermal gravimetry analysis (TGA) (Perkin Elmer-TGA-4000) in college of science, university of Muthanna. at the heating rate 20 C /min in Temperature range (40-605) under nitrogen atmosphere with flow rate of 20ml/min and Differential Scanning Calorimetric (DSC) analysis in college of Engineering, University of Tehran. at the heating rate 10 C /min in Temperature range (0-600) 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 surface morphology was examined from scanning electron microscopy (SEM) and Transmission Electron Microscope (TEM) in college of Engineering, University of Tehran

2.3. Methods:

2.3.1. Nanomagnetic IPN's:

Nanomagnetic particles (Fe_3O_4), poly thiourea-formaldehyde were separately synthesized according to the references [11,12] respectively. A new [(cured epoxy resin - poly thiourea- formaldehyde) nanomagnetic full- IPN's] (NM full IPN's) was prepared by mixing nanomagnetic particles (Fe_3O_4) and the epoxy resins/hardener (1:0.5) and polythiourea- formaldehyde with weight ratio of (0.1:1:1). 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 mould and kept in oven at 70 °C for 24 hrs [13] (Fig.1) .

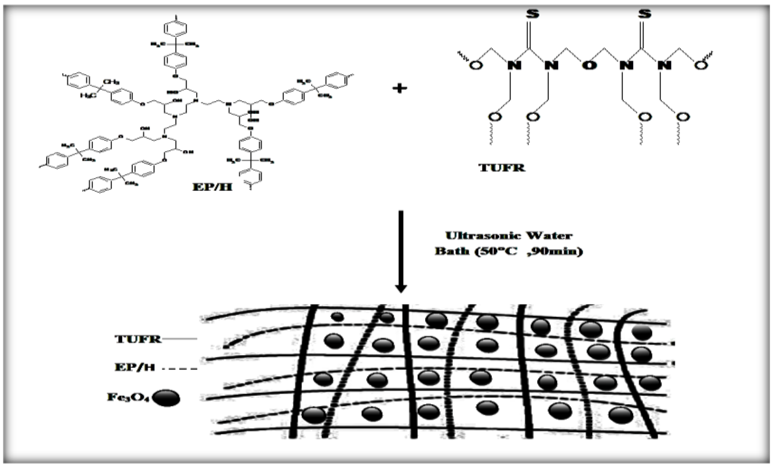

Figure 1. Mechanism of formation for (NM Full- IPN's)

2.3.2. Adsorption Experiments

The adsorption behavior of the new nanomagnetic full- IPN's for metal ions (Cd^{2+} and Pb^{2+}) was investigated using batch system. 10 mg/L of each metal ion was mixed with 0.05g of the nanomagnetic full-IPN's (adsorbent) with continuous shaking at 180 rpm for different times (10, 20, 30, 60, 120 min and 24 h) and different PH (2,4,6 and 8).The pH of solution was adjusted HCl and NH_4OH. After attaining the adsorption equilibrium, all these mixtures were filtered. Filtrates were by flame atomic absorption spectrophotometer to determine the concentration of ions (Cu^{2+}, Cd^{+2}, Pb^{2+}) at wavelengths (228.8, 283.31) nm, respectively. The equilibrium adsorption capacity, qe (mg /g) and the percentage removal of metal was calculated using the mass balance, according to the equations[14-17]:

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

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

2.3.3. Study of Adsorption Isotherms

A 10 ml of each ion solution (Cu^{2+}, $Cd^{2+}$and pb^{2+}) with different concentrations (1, 10, 20 and 30) ppm were used to study of adsorption isotherm with nanomagnetic full- IPN's. Langmuir isotherms were plotted by using its standard straight-line equation (2) [14-17]:

$$\frac{1}{q} = \frac{1}{bq_mC_e} + \frac{1}{q_m} \cdots\cdots\cdots\cdots\cdots (2)$$

Where ‘q’ (mg g-1) is the amount of metal ions adsorbed, ‘C_e’(ppm) is the concentration of metal at equilibrium, qm (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 isotherms were plotted using following standard straightline equation (3) [14-17]:

$$\log q = \log K_F + \frac{1}{n}\log C_e \cdots\cdots\cdots\cdots (3)$$

3. Results and Discussions:

3.1. Characterization:

3.1.1. FTIR Spectroscopy:

The IR spectrum the new [(cured epoxy resin - poly thiourea- formaldehyde) nanomagnetic full-IPN's**]** (NM full IPN's) are shown in Fig.2. A broad band at 3425 cm^{-1} can be assigned to the O–H stretching vibration. while the bands absorption in the range (3000 -2850 cm^{-1}) are due to the CH_2, CH_3 symmetric and asymmetric stretching and banding, respectively (18,19), also absorption bands at 1604 cm^{-1} and 1504 cm^{-1} assigned to the aromatic C=C stretch (18,20). Moreover, signals located in the range (1300–1050) cm^{-1} can be assigned to C–N, C–C and C–O stretching (18-21), On other hand, the absorption bands at (1570-1395) cm^{-1}, (1420-1260) cm^{-1} and (1140-940) cm^{-1} and due to mixed vibrations C=S and –N-C=S groups of TUFR (23-27) . Also showed that the broad band signal at 578 cm^{-1} due to the Fe-O for magnetic nanoparticles (28-32).

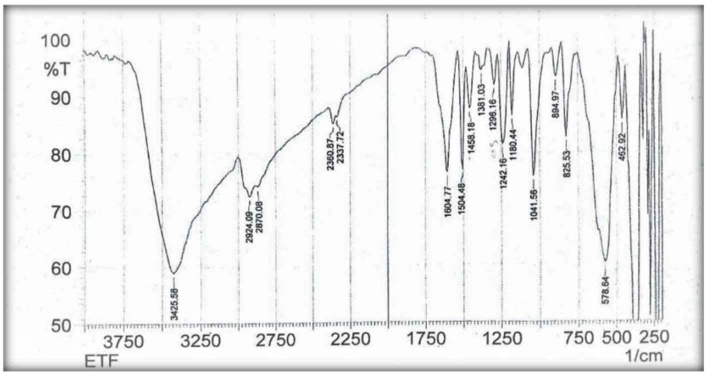

Figure 2. IR Spectrum of (NM Full- IPN's)

3.1.2. Thermal Analysis

The thermal stability of NM full IPN's was evaluated by thermogravimetric analysis (TGA) and differential thermogravimetric (DTG). Fig.3(a) TGA curves showed three process stages for decomposition of NM full IPN's with different weight loss at different temperatures , the 1st stage can be related to the evaporation of solvent (water) and low molecular weight resin the main degradation (2nd stage) has occurred at 377°C with weight loss (33.4%) due to the degradation of crosslinked materials, while the final degradation stage (3rd stage) has occurred at 765°C with Wight loss 21% and showed good char residue content., the network of epoxy resins had been destroyed partially and molecular chains were broken, thus leading to the formation of smaller molecules such as Bisphenol A , Hydroxybenzene Olefin and Ketone. While the thiourea- formaldehyde network had been decomposing by cleavage of C=S, C-N and C-O bonds to the formation of small fragments. The DSC thermograms of cured prepared nanomagnetic IPN's shown in Fig 3 (b) and showed that the endothermic peak was most likely due to the vaporization of water. This was in agreement with the TGA results and the degradation process has been very clear as exothermic peak in DSC thermograms for IPN's.

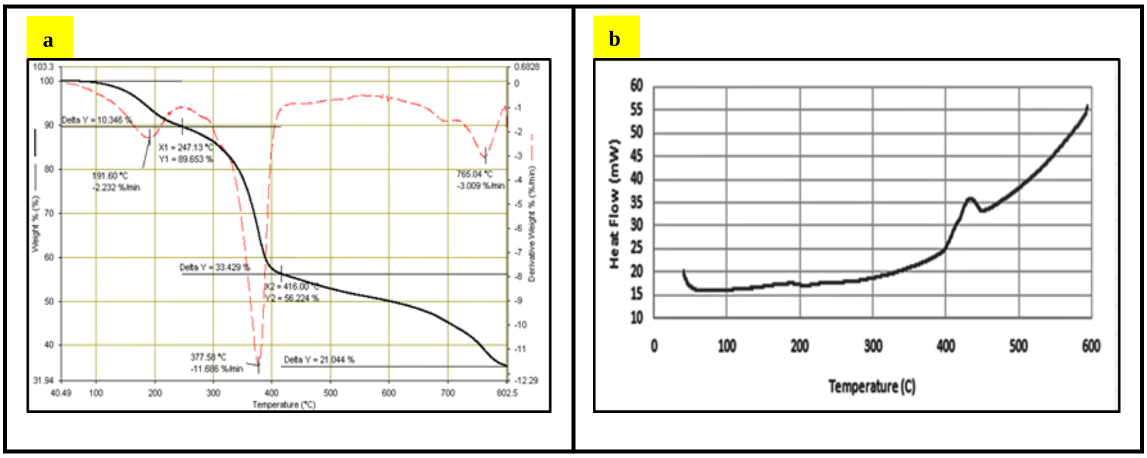

Figure 3.TGA and DTG curves(a) and DSC curves (b) of (NM-Full IPNs)

3.1.3. Surface morphology:

The size and morphology structure of (NM Full- IPN's) was studied by SEM and TEM. Fig 4. shows the SEM and TEM images of (NM Full- IPN's) clearly has a spherical morphology with diameter 37nm and that the Fe_3O_4 nanoparticles edges were brighter than the center of the nanoparticles, suggesting the particles were encapsulated by IPNs.

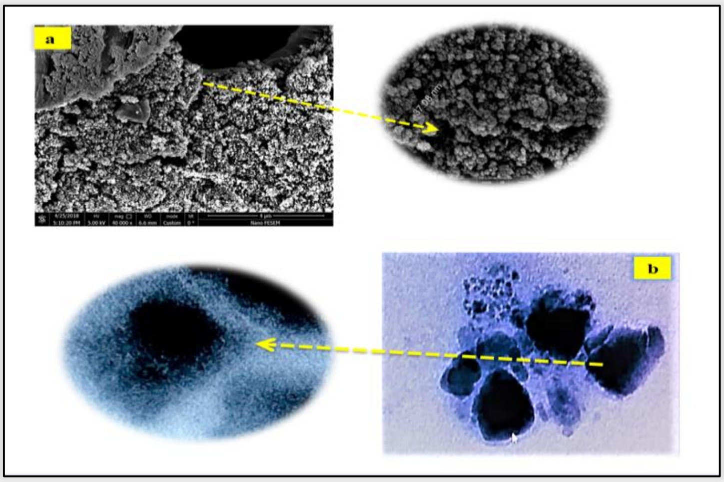

Figure 4. SEM Images (a) and TEM Images (b) of (NM Full- IPN's)

3.2s Analytical Study:

3.2.1. The e effect of pH on removal metal ions[33-35]:

The pH value of the aqueous solution is an important controlling parameter in the adsorption process. These pH values influence the surface charge of 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 full IPNs) studies with an initial concentration of 0.05 g at room temperature with different contact time for solutions from Cu(II),Cd(II)and pd(II) . The effect of pH on the adsorption capacity followed a similar trend Fig5. 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, 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 surface were protonated, which would cause a cationic repulsion between the metal ions and the active sites 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 to form metal hydroxide.

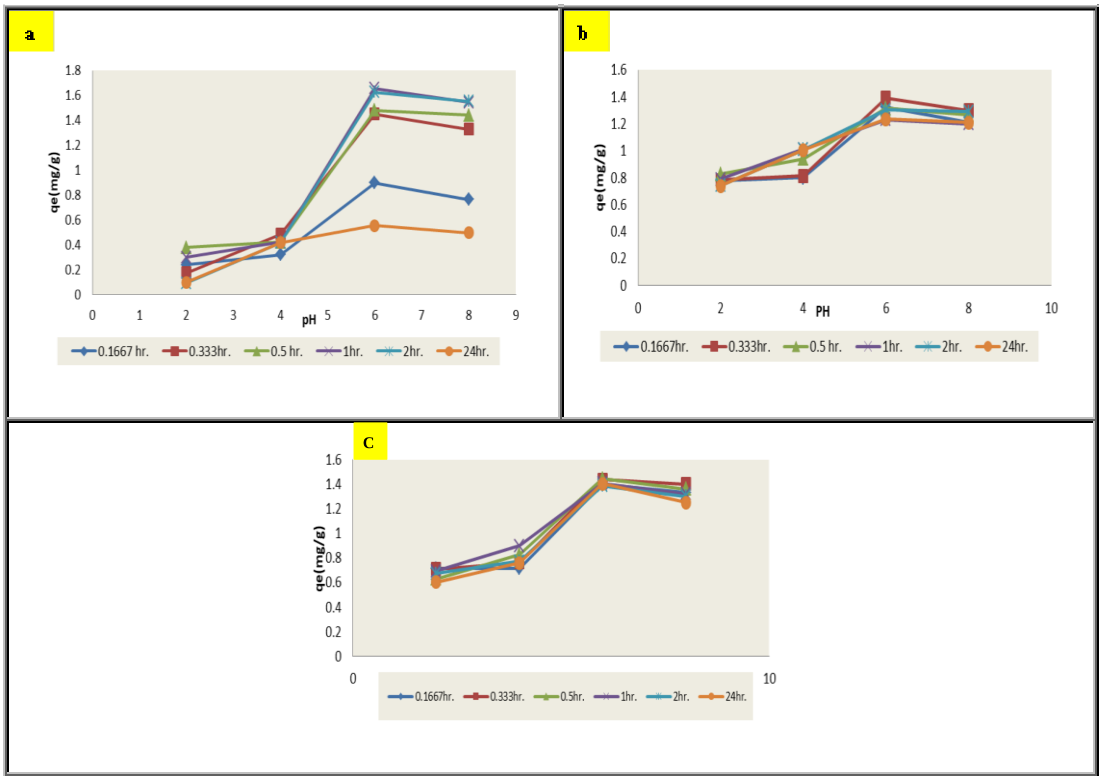

Figure 5. Effect of pH on metals redr1qqqqqqqmoval by (0.05 g of NM full IPNs): (a) pb^{2+} (b) Cd^{2+} (c) Cu^{2+} at 25 °C and different time

3.2.2. Effect of time 40-4.

The equilibrium adsorption capacityof Cu(II), Cd(II) and Pb(II) on surface (NM semi IPN's)as a function of contact time are shown in Fig.6. The adsorption rate is rapid in the beginning due to more active sites available on polymer and gradually decreases until equilibrium state is reached due to occupancy of active sites of adsorbent.

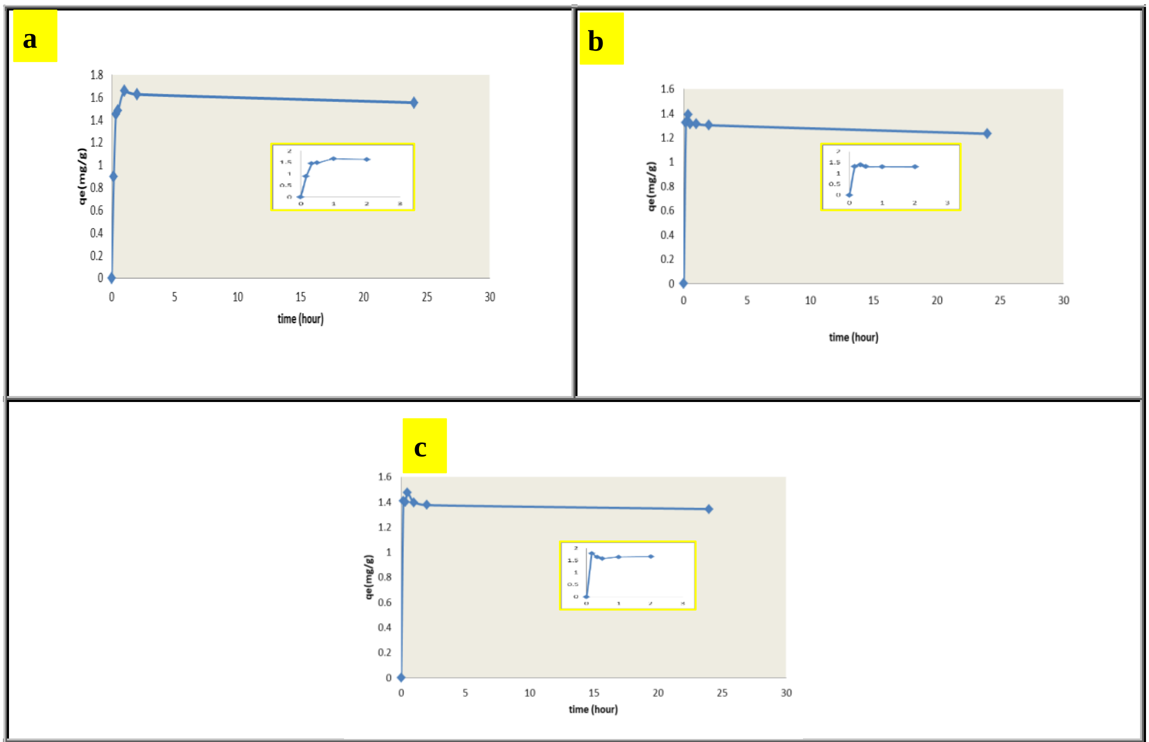

Figure 6. Effect of contact time on metals removal by (0.05 g of NM full IPNs): (a) pb^{2+} (b) Cd^{2+} (c) Cu^{2+} at 25°C

3.2.3. 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), optimum pH=6 and optimum shaking time for capacity adsorption of all metal in this study. The Langmuir and Freundlich isotherms parameters were shown in Tables 1. According to the coefficients of correlation obtained from linear regression, it was found that in all cases the Langmuir model fit 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 (Cu(II) ,Cd(II) and ,Pb (II)) from the solutions on the surface (NM full IPN's) 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. 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[36-38]
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Table 1: Parameters of Freundlichand Langmuir Constants for Adsorption

Metal ion	Freundlich Isotherm Parameters			Langmuir Isotherm Parameters		
	1/n	KF	R^2_F	Qm (mg g^{-1})	b (L g^{-1})	R^2_L
Pb^{2+}	7.987	6.098	0.853	2.564	1.423	0.898
Cd^{2+}	1.117	0.629	0.999	6.944	0.0438	0.999
Cu^{2+}	1.058	0.539	0.892	1.628	0.126	0.981

Table 2: Comparsion of Maximum Adsorption Capacity of (NM Full 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
Raw pomegranate peel	Cu (II)	1.3185	41
Sugarbeet pulp	Cu (II)	0.15	42
Amberlite	Cd(II)	0.640	43
polyaniline/polypyrrole nanoparticles Type 2 Type 3 Type 4	Cd(II)	0.261 0.345 0.639	44
chromium doped nickel nano metal oxide	Cd(II)	0.1119	45

4. Conclusion:

The results of this study indicates that (NM full IPN's) can be successfully utilized for removal of Cu (II) , Cd(II) and Pb(II) from aqueous solution .The metals adsorption were tested at different conditions such as contact time and initial pH .The optimum solution pH for Cu (II) , Cd(II) and Pb(II) from aqueous solution was found to be 6 .The sorption of Cd(II) and Pb(II) by (NM full IPN's) followed a monolayer sorption model langmiur isotherm rather than multilayer model .

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