Selective adsorption of Cu(II) from synthetic wastewater using melamine-formaldehyde-NTA resin

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Abstract

A new chelating resin was prepared by anchoring the chelating agent nitriloaminetriacetic acid (NTA) to melamine via an amide covalent bond during melamine-formaldehyde condensation reaction in an acidic medium. The effect of preparation conditions (temperature, acidity, and water content) on resin characteristics (water regain, rigidity, NTA functionality, and porosity) were monitored to specify the best preparation conditions. A pH of 1.3, temperature of 150°C and water content of 5 ml were found as the best conditions for resin preparation with stated amounts of reactants. This new resin was chemically characterized via infrared spectroscopy (FT-IR), CHNO elemental analysis, and morphologically characterized via nitrogen gas adsorption (BET) and field emission-scanning electron microscopy (FE-SEM). The best-produced resin sample has a surface area of 159 m^2/g. The content of NTA was about 1.24 mmole/g. Simultaneous adsorption of Co(II), Cd(II), Zn(II), and Cu(II) from synthetic wastewater solutions using a batch technique was quantitatively analysed using atomic absorption. Selective adsorption of the Cu(II) ion amongst Co(II), Cd(II), and Zn(II) ions by this resin was noted. It was found that Cu(II) adsorption is spontaneous ($\Delta G_{ads} < 0$), exothermic ($\Delta H_{ads} < 0$), and reversible ($\Delta S_{ads} < 0$). Kinetically, it follows reversible and pseudo first-order. According to the Langmuir model, the capacity for Cu(II) adsorption is 52.6 mg/g (0.83 mmol/g). EDTA solution can regenerate the resin by stripping adsorbed metal ions. After regeneration, it was observed that the capacity decreased and this may be due to partial hydrolysis of NTA sites.
Keywords: melamine-formaldehyde-NTA resin, selective adsorption, heavy metals, kinetics, isotherm, thermodynamics.

1   Introduction

Environmental contamination by heavy metals seriously threatens human health because of its high toxicity. Mining, metal plating, tanneries, nuclear power plants, industrial emissions, agriculture and domestic activities are examples of such contamination sources. Conventional techniques for the removal of heavy metals from wastewater effluents are chemical precipitation, ion exchange, electrodialysis, membrane separation, solvent extraction and adsorption. Different types of adsorbing materials are used for removing heavy metals from wastewater such as zeolites, biosorbents, active carbon and polymeric resins.

The aim of this work is to produce a chelating resin and investigate its simultaneous removal behaviour against selected heavy metals [Cu(II), Co(II), Cd(II) and Zn(II)]. Only a few studies describe the simultaneous metal ions removal (Machida *et al* [3]). MF-NTA chelating resin was synthesised by anchoring NTA to the MF matrix where carboxylic groups of NTA react with primary amine groups of melamine forming amide bonds [1, 2]. The effects of different parameters (solution initial pH, temperature, metal ions initial concentration and contact time) on adsorption were considered. As Cu(II) showed selective adsorption, its experimental adsorption data was fitted to selected adsorption kinetics and isotherm models. The thermodynamic parameters (adsorption free energy, enthalpy and entropy) were also calculated.

2   Theory

2.1   Resin preparation (chemistry of reaction)

MF-NTA resin was synthesised under acidic conditions. In the course of resin formation, methylol groups (triazine−NH−*CH₂OH*) are formed from reaction of formaldehyde with amine groups. Subsequently, the methylol groups condense to form methylene and ether bridges constructing the resin matrix [4, 5]. During MF matrix formation, NTA molecules are anchored to the matrix by forming amide covalent bonds (Sharmin *et al* [6]).

2.2   Resin characterization

The water amount held intrinsically by the resin represents the water regain factor. To calculate this factor, eqn (1) was employed:

$$W\% = 100(W_{\mathrm{w}} - W_{\mathrm{d}}) / W_{\mathrm{w}} \tag{1}$$

where W_{w} and W_{d} are weights (g) of the wet and dried resin respectively. Characterization using IR spectroscopy, CHNO elemental analysis (MF-NTA and MF resins), N_2 adsorption/desorption analysis using BET method and SEM imaging (MF-NTA resin only) were carried out.

2.3   Metals adsorption

Adsorption kinetics, thermodynamics and isotherm studies characterize the adsorption behaviour of a resin towards heavy metal ions and give an understanding about the adsorption mechanism. To reveals these characteristics, essential parameters have to be considered such as the initial pH, temperature, time of contact and initial concentration of the metal ions. In this study, pH values above 6 were avoided because of probable metal hydroxide formation which may give spurious adsorption results [7-9]. Metals under study [Co(II), Cd(II), Zn(II), and Cu(II)] were subjected to competitive adsorption process where all ions were present in the batch solutions with the same initial mass concentration. Sodium (I) ion, as sodium chloride, was present as well in solution representing salt matrix.

For selectively removed Cu(II), the adsorption kinetics was studied using two conventional models: reversible first-order and pseudo first-order [10, 11]. The reversible first-order has the following linear form, eqn (2):

$$\ln(1 - U_t) = \ln(1 - x / X_e) = -kt \tag{2}$$

where $U_t = x/X_e$ (x is the concentration of solute adsorbed on resin at certain time and X_e is the concentration of solute adsorbed at equilibrium). The overall adsorption rate constant (k) equals $k_1 + k_2$, where k_1 and k_2 are the forward (adsorption) and backward (desorption) rate constants respectively. To calculate these parameters, the auxiliary eqn (3) was used:

$$K_c = X_e /(C_i - X_e) = k_1 / k_2 \tag{3}$$

where K_c is the equilibrium constant and C_i is the initial ion concentration. The integrated form of the pseudo first-order equation is expressed by eqn (4):

$$\log(q_e - q_t) = \log q_e - (k_{ad} / 2.303)t \tag{4}$$

where q_e and q_t are the solute amounts adsorbed by the resin (mg/g) at equilibrium and time t respectively and k_{ad} is the adsorption rate constant (min^{-1}). To calculate the thermodynamic parameter (ΔG_{ads}) (free energy of the adsorption process), eqn (5) was employed:

$$\Delta G_{ads} = -RT \ln K_c \tag{5}$$

By plotting ln K_c against $1/T$, ΔH_{ads} and ΔS_{ads} (enthalpy and entropy of adsorption) can be calculated from the slope and intercept of eqn (6):

$$\ln K_c = (\Delta S_{ads} / R) - (\Delta H_{ads} / RT) \tag{6}$$

Two adsorption isotherm models were employed in this study, the Freundlich and Langmuir. The Freundlich model is the one that is usually used for aqueous systems and assumes a heterogeneous surface where the adsorption sites have different energies (Faust and Aly [12]). It has the following linear form, eqn (7):

$$\log q_e = \log K_F + (1/n) \log C_e \tag{7}$$

where q_e (mg/g) is the adsorbed amount at equilibrium, C_e (mg/l)is the concentration at equilibrium. The terms K_F and n are Freundlich parameters which are related to adsorption capacity and adsorption intensity respectively. The Langmuir model was earliest to describe adsorption phenomena. The basic assumptions for this model may be applicable to MF-NTA resin (definite sites, monolayer accommodation of solutes and sites have the same adsorption energy) Faust and Aly [12]. The Langmuir model linear equation has the following form, eqn (8):

$$1/q_e = 1/Q_o + 1/bQ_oC_e \qquad (8)$$

where, q_e and C_e have the same meaning as for the Freundlich model. The terms Q_o (mg/g) and b (l/mg) are Langmuir model parameters. Q_o represents the adsorption capacity and b is related to energy of adsorption and reflects the affinity of the metal ion towards binding sites. The dimensionless factor, R_L, indicates whether the adsorption is favourable or not (Adsorption is favourable if $0<R_L<1$). It is defined by eqn (9):

$$R_L = 1/(1 + bC_i) \qquad (9)$$

2.4 Resin regeneration

EDTA solution can regenerate exhausted MF-NTA resin by stripping the chelated metal ions into aqueous solution forming stable soluble M(II)-EDTA complexes.

3 Experimental

3.1 Preparation of resin (condition optimization)

Analytical grade of melamine (99%) (Aldrich), formaldehyde (38%) (BDH), NTA (Sigma) were used for MF-NTA and MF resin preparation. For all preparations, deionised water was used. Twelve MF-NTA resin samples were prepared. All had the same reactant amounts: 0.01 mole melamine (1.26 g), formaldehyde (2 ml), and 0.003 mole NTA (0.64 g). For each sample, the following procedure was carried out. Melamine was added to NTA in a vial containing certain amount of acidified water (5 ml or 10 ml). The water acidity (pH 1.5 or 1.3) was pre-adjusted using concentrated HCl. Finally formaldehyde was added and the reactants were mixed by an electronic agitator to ensure formation of homogenous slurry. The tightly closed vial then was put in a preheated oven at a specified temperature (90, 120 or 150°C). The formed solid resin was left for an extra 30 minutes at the same preparation temperature for more curing. The vial was then removed and left on a bench over night. The sample was then ground and sieved. The grains in the range of 355 to 710 μm were washed in 100 ml deionised water for 30 minutes five times at ambient temperature using a shaker at 150 rpm to remove acidity and any other excess reactant (melamine, NTA, and Formaldehyde). The washed sample was stored in

clean tightly-closed vial until characterization tests. From these twelve samples, the one with highest surface area and good mechanical strength was used for a series of metal adsorption experiments.

3.2   Resin characterization

For water regain determination, resin samples were centrifuged for three hours at 1000 rpm to remove excess water and then weighed (W_w). These samples were then dried at 50–60°C until complete dryness then weighed again (W_d). Eqn (1) was then used to determine water regain factor. Freeze dried sample was required for BET analysis and SEM imaging and this was carried out by freezing the sample at −80°C then evaporating the water under low pressure (0.06 atm.). IR analysis was carried out (KBr discs) in the range 400 to 4000 cm^{-1} using a Perkin-Elmer FT-IR spectrometer. Dried samples were used for CHNO elemental analysis using Perkin-Elmer Series II CHNS/O Analyser model 2400. The Micromeritics ASAP 2405N adsorption analyzer was used for measuring nitrogen adsorption/desorption isotherms at 77.4 K to determine porosity characteristics of the freeze dried samples. Field Emission-Scanning Electron Microscope (FE-SEM) was employed for imaging the outer surface of a freeze dried grain of a selected resin sample to elucidate the morphology and porosity.

3.3   Metal ions adsorption

Analytical grade of $CuCl_2.2H_2O$ (May & Baker LTD), $CoCl_2.6H_2O$ (BDH), $ZnCl_2.2H_2O$ (Fisher Scientific), $CdCl_2.2.5H_2O$ (Sigma-Aldrich) were used for the preparation of standard stock solutions (1000 ppm and 1% HCl) for each element using deionised water. Standard diluents were freshly prepared from these stock solutions for adsorption experiments. Standard diluents were pH-adjusted using concentrated and diluted HCl and NaOH. The batch adsorption technique was conducted for examining the adsorption behaviour and the essential factors considered for study were pH (3, 4, 5 and 6), temperature (15, 20, 25, 30 and 35°C), contact time (10, 20, 30, 40, 50, and 60 minutes) and metal-ions initial concentrations (20, 30, 40, 50, 60 and 70 ppm). It is important to state that initial concentrations of these metals are different on a molar basis. Other parameters were set constant, shaking speed (200 rpm), grain size (355–710 μm), solution volume (50 ml) and wet resin dose (0.3 g). Also, in all experiments except isotherm one, 20 ppm of Na (I) ion was present representing the salt matrix effect. The adsorption was tested by measuring the ion concentrations after the adsorption process using the Perkin-Elmer atomic absorption spectrometer 3100 with multi-element hollow cathode lamps and an air-acetylene burner was used for determining the residual metal ion concentrations. The wave-lengths (nm) applied were those recommended by the manufacturer and were as follows: Co(II) 240.7, Cu(II) 324.8, Cd(II) 228.8, and Zn(II) 213.9.

   The effect of initial pH was investigated by carrying out the adsorption process at different five temperatures (15, 20, 25, 30 and 35°C). For each temperature, four flasks (each flask at certain initial pH value: 3, 4, 5 and 6) with

metal-ion initial concentrations of 20 mg/l were shaken for 120 minutes. From each flask, 5 ml was withdrawn and residual metal-ion concentrations were measured. An adsorption isotherm study was carried out by shaking six flasks with different initial concentrations (20, 30, 40, 50, 60 and 70 mg/l) at 20°C and an initial pH of 5. From each flask, 5 ml was withdrawn to measure the residual metal-ion concentrations. The kinetics of adsorption (60 minutes duration) was studied at 20°C for different pH values (3, 4, 5, and 6). From each flask, 3 ml was withdrawn each 10 minutes and residual metal-ion concentrations were measured.

3.4 Regeneration of MF-NTA resin

50 ml of EDTA solution (0.1 M) was used to regenerate 0.3 g of exhausted MF-NTA resin by shaking the resin dose for 30 minutes at 200 rpm and at room temperature. The resin dose was then washed five times each with 50 ml of deionised water to remove any residual of EDTA. The regenerated resin mass was then used for a second adsorption experiment.

Table 1: Gelling time, Water regain, elemental composition and rigidity of MF-NTA resin samples.

Temp. (°C)	Water content	pH	G.T.[a]	W %	R[b]	Experimental C : H : N : O	No.
90	5	1.5	67	65	A	34.5:5.19:41.35:18.9	1
		1.3	60	80	A	34.9:5.19:40.73:19.2	2
	10	1.5	75	86	C	---------	---
		1.3	107	83	D	---------	---
120	5	1.5	10	78	A	34.8:4.68:40.85:19.65	3
		1.3	20	78	B	34.87:4.87:41.58:18.7	4
	10	1.5	36	82	D	---------	---
		1.3	110	81	C	---------	---
150	5	1.5	17	72	A	34.74:4.92:40.45:19.99	5
		1.3	21	77	A	35.1:4.84:40.03:20.03	6
	10	1.5	45	90	C	---------	---
		1.3	71	75	D	---------	---
MF resin	---	---	---	---	---	*31.7:5.6:41.4:21.2*	---

[a] G.T. (Gelling Time), [b] Rigidity type: A(very hard), B (hard), C (fair hard), D (soft)

4 Results and discussion

4.1 Resin characterization

4.1.1 Gelling time, Water regain, rigidity, and elemental analysis of the resin

The samples showed gelling time ranges from 10 to 110 minutes (Table 1). Samples with water content of 10 ml had the higher gelling time. The higher water content increase spacing between reactants and this gives more time for matrix formation. Water regain (≈ 77%) shows the hydrophilicity of this resin

which is due to the presence of carboxyl functional groups in the resin and this percentage suggests that the resin is rich in NTA. The elemental analysis of all samples gave almost the same C:H:N:O ratio indicating same chemical structure. This ratio is different from that of MF control resin due to modification by NTA. From calculation, NTA constitutes 24% of the resin mass (1.24 mmole per gram dry resin). It was noted that samples with the higher water content are less rigid due to increase of spacing in the matrix. Samples classified as A and B (for rigidity) in Table 1 were chosen for porosity characterization by the BET method.

4.1.2 IR spectra

IR spectra of all twelve MF-NTA samples (not shown) are very similar which indicates that all samples have the same chemical structure. Comparing one of these spectra against the MF resin spectrum, as shown in Figure 1, shows some important differences due to anchoring NTA. For MF-NTA spectrum, the amide (and/or carboxylic) carbonyl (C=O) stretch appeared at 1636 cm^{-1} and the carboxylic O–H in plane bend appeared at 1390 cm^{-1}.

4.1.3 Porosity (BET characterization)

The basic porosity characteristics of MF-NTA resin samples are given in Table 2. All samples have insignificant porosity in the micropore range compared to BET surface area which is desirable from the metal-ion adsorption point of view. Nitrogen adsorption/desorption hysteresis loop of sample No. 6 (Figure 2) indicates an open pore structure (Do [13]). The dark spots seen in FE-SEM image of MF-NTA resin (Figure 3) represent the pore openings and cavities. This open structure enhances adsorption kinetics. Sample No. 6 shows the highest surface area (159 m^2/g) and the adsorption experiments were conducted using it.
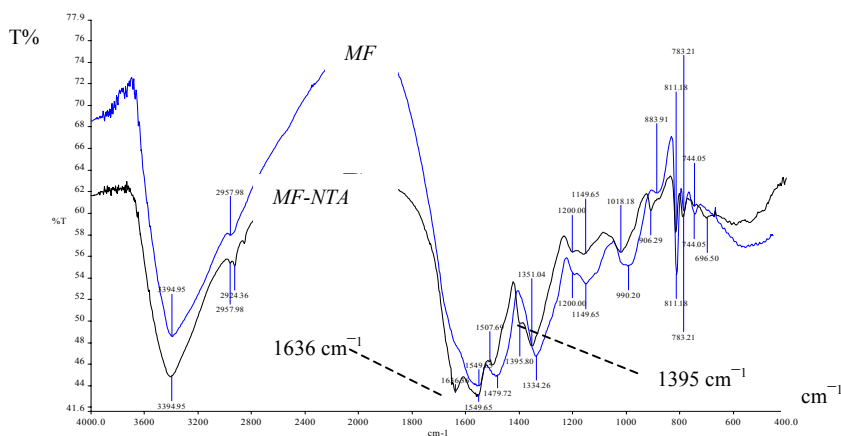

Figure 1:   IR spectra of *MF* and *MF-NTA* resins.

Table 2:   Porosity parameters for six selected samples (No. 1-6).

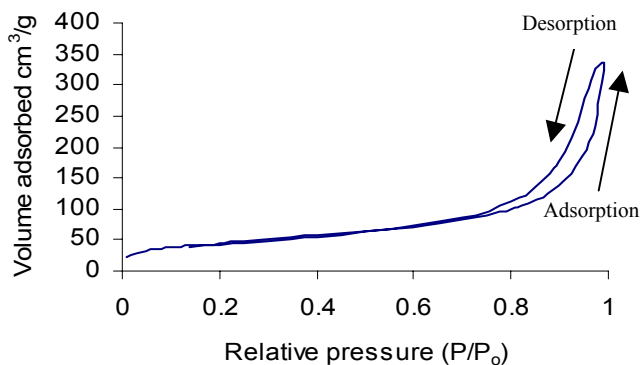| No.	BET surface area, m^2/g	Micropore area, m^2/g	BJH Adsorption Cumulative Pore Volume, cm^3/g	Average pore diameter, Å
1	90.7383	6.3344	0.364929	158.7561
2	102.1936	3.9713	0.356313	137.6444
3	94.2898	6.6269	0.337655	140.9535
4	14.8005	1.4088	0.058127	127.6997
5	142.7730	9.0602	0.483588	133.2255
6	159.3630	8.7384	0.528643	130.4835

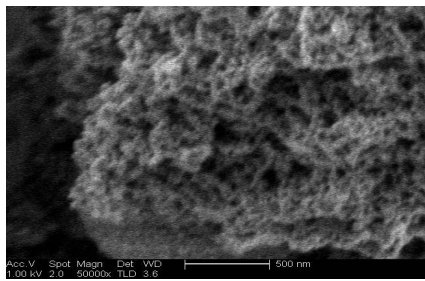Figure 2:   The adsorption/desorption loop of MF-NTA, sample No.6.

Figure 3:   FE-SEM surface image of MF-NTA, sample No. 6.

4.2   Adsorption process

4.2.1 Effect of pH and temperature (thermodynamics)

The experiments at different initial pH values (3, 4, 5 and 6) and various temperatures (15, 25 and 35°C) indicated that adsorption of Cd(II) and Zn(II) is negligible under these conditions whereas Cu(II) and Co(II) show adsorption.

For each temperature, the adsorption *increases slightly* with initial pH and for each initial pH value, there is a *notable decrease* in adsorption with temperature for Cu(II) and Co(II). Cu(II) showed higher adsorption over Co(II) for all conditions. The highest measured adsorption for Cu(II) is about 67% of initial concentration (about 30% for Co(II)) and these moderate percentages may be due to using small amount of resin (0.3 g of wet resin corresponds to a solid fraction of 0.069 g). Table 3 gives adsorption free energies for Cu(II) for different conditions. These are negative which reflects the spontaneous process and it is noticed that as temperature decreases, the free energy becomes more negative. This means that adsorption is favourable at lower temperature. Plots of $\ln K_c$ against $1/T$ for Cu(II) at pH 3, 4, 5, and 6 were generated from which adsorption thermodynamic parameters ΔH_{ads} and ΔS_{ads} were calculated. Table 4 shows these parameters. The negative enthalpy corresponds to exothermic process and *chelation adsorption* is likely to be the main mechanism. The negative value of entropy means a decrease in randomness which can be attributed to formation of metal ion chelates (restriction of metal ions) accompanied by the accommodation of released water molecules (upon chelate formation) on resin hydrophilic surface. It also reflects the reversibility of the process.

Table 3:   Adsorption free energy, ΔG_{ads} (kJ mol^{-1}).

Temp. (°C)	pH 3	pH 4	pH 5	pH 6
15	−1.09	−1.38	−1.52	−1.56
20	−0.97	−1.17	−1.28	−1.64
25	−0.50	−0.97	−1.22	−1.21
30	−0.53	−0.68	−0.76	−1.06
35	−0.38	−0.67	−0.67	−0.82

Table 4:   Adsorption thermodynamic parameters ΔH_{ads} and $\Delta S_{ads.}$

pH	3	4	5	6
ΔH_{ads} (kJ mol^{-1})	−11.43	−11.74	−13.34	−12.54
ΔS_{ads} (J mol^{-1} K^{-1})	−35.97	−36.03	−41.03	−37.72

4.2.1 Adsorption kinetics

Adsorption time profiles at temperature 20°C for Cu(II) (over a time range of 60 minutes) for different pH values were determined and indicates that removal rate is high (the half load time, $t_{1/2}$ [Cu(II)]=12, 10.7, 11.4 and 10.3 minutes for pH 3, 4, 5 and 6 respectively). Pseudo first-order and reversible first-order plots were generated from which the constants were calculated (Table 5). The values of k_{ad} are very similar to the corresponding values of k. $k_1/k_2 >1$ for Cu(II) which means that process shifts to adsorption direction. Both models are able to represent the adsorption of Cu(II) as the values of correlation factor (R^2) indicate.

Table 5: Rate constants (min^{-1}) of pseudo and reversible first order kinetics.

pH	Pseudo first-order		reversible first order			
	k_{ad}	(R^2)	k	(R^2)	k_1	k_2
3	0.107	(0.9875)	0.104	(0.9912)	0.064	0.040
4	0.102	(0.9794)	0.105	(0.9820)	0.065	0.040
5	0.115	(0.9892)	0.112	(0.9885)	0.068	0.043
6	0.091	(0.9839)	0.090	(0.9852)	0.057	0.033

4.2.2 Adsorption isotherm

The adsorption isotherm for Cu(II) at 20°C and pH 5 shows that q_e increases significantly with C_e. Plots of this adsorption isotherm data according to the Langmuir and Freundlich models were generated and constants were calculated (Table 6). The value of the Freundlich parameter, $1/n$, corresponds to favourable adsorption. The other Freundlich parameter, K_F, indicates high capacity [7, 8, 11]. The Langmuir parameter, $Q_\circ$, was found to be 52.6 mg/g (0.83 mmole/g). R_L is in the range of favourable adsorption. The Langmuir correlation factor (R^2) is slightly higher than that for Freundlich model which may mean more homogeneity of the surface.

Table 6: Adsorption isotherm constants of Freundlich and Langmuir for Cu(II).

Freundlich			Langmuir			
K_F	$1/n$	R^2	$Q_\circ$	b	R_L	R^2
2.65	0.68	0.9956	52.6	0.032	0.61	0.9968

4.3 Regeneration and recycling of MF-NTA resin

The regeneration process succeeded in renewing the resin to about 91% of its original capacity. The release of NTA into treated wastewater or during regeneration due to partial hydrolysis may be the reason of decrease in capacity [1]. After complete exhaustion (several regeneration cycles), the resin can be incinerated to form porous carbon material which in turn can be used for a variety of applications.

5 Conclusions

The optimum conditions for the preparation of melamine-formaldehyde-NTA (MF-NTA) resin are a pH of 1.3, temperature of 150°C, and water content of 5 ml with the stated amounts of reactants. IR, elemental analysis proved the success of anchoring NTA to the MF matrix via amide bonds. The produced resin has high hydrophilicity (water regain 77 %) with a surface area of 159 m^2/g. Calculations show that 1.24 mmole of NTA is present per gram of solid resin. The removal of Cd(II) and Zn(II) was negligible at all conditions but

Cu(II) and Co(II) showed considerable removal and this may be due to limited sites present in resin dose with respect to total heavy metal ions concentration. The priority of Cu(II) and Co(II) for adsorption over Cd(II) and Zn(II) may be attributed to their chelate formation constants. The removal is 67% for Cu(II) and 30% for Co(II). For Cu(II), adsorption process is spontaneous ($\Delta G_{ads} < 0$), exothermic ($\Delta H_{ads} < 0$), and reversible ($\Delta S_{ads} < 0$). The exothermic adsorption suggests chelation of ions to NTA sites present in the resin to be the mechanism of adsorption. The rate of adsorption is considerably high ($t_{1/2}$ is within minutes). The adsorption obeys both reversible and pseudo first-order models. According to the Langmuir model, the capacity, ($Q_\circ$) for Cu(II) is 52.6 mg/g (0.83 mmol/g). The Langmuir model gave a better fit to the experimental data suggesting more homogeneity of the surface. The Cu(II) ion was selectively removed from aqueous solution of the mixed four ions [Cu(II), Co(II), Cd(II) and Zn(II)] by MF-NTA resin. Similar resins can be prepared using different polyamine-polycarboxylic acids (e.g. DTPA and CDTA) and can present different adsorption behaviour towards heavy metals.

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