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Preparation of Polyacrylonitrile Functionalized Melamine Resin and Investigation of its Metal ions Adsorption Behavior

MEHDI HOSSEINZADEH^{1*} AND FARIDEH MAHMOODZADEH²

¹Marand Faculty of Technical and Engineering, University of Tabriz, Tabriz, Iran

²Halal Research Center of IRI, FDA, Tehran, Iran

ABSTRACT

A novel functional resin, polyacrylonitrile-melamine (CPAN-M), was made through the nucleophilic addition reaction of cross-linked polyacrylonitrile (CPAN) with melamine. It was developed for the removal of Cu (II), Pb (II) and Zn (II) from aqueous solution. The sorption experiments were investigated by synthesized functional resin under different experimental conditions, such as temperature, initial concentration, pH and contact time. The results showed that the adsorption behavior of the resin for selected metal ions was found to be greater at higher pH values. The high adsorption rate (<20 min) was seen. The maximum adsorption capacity on CPAN-M was determined as 123 mgg⁻¹ for Cu (II). The adsorption kinetics followed the pseudo-second-order equation, while the adsorption isotherms were well fitted for the Langmuir model. The desorption experiments by elution of the obtained resin with a hydrochloric acid (HCl) show that the CPAN-M could be reused. The prepared resin and its metal chelates were characterized by Fourier transform infrared Spectroscopy (FT-IR), elemental analysis, thermogravimetric analysis (TGA), gravimetry, UV- vis spectroscopy, and atomic absorption techniques (AAS).

KEYWORDS : Polyacrylonitrile, Melamine, Chelating resin, Metal ions, Adsorption.

1. INTRODUCTION

With the advent of new technologies and rapid development of the global industry, heavy metal ions are increasingly discharged into the environment^[1]. Unlike some organic pollutants,

heavy metals cannot be decomposed or metabolized, thus hazardous to the ecological environment and can also easily enter the food chain and cause various diseases^[2, 3]. Therefore, there is need to remove and recovery

of heavy metal ions from the environmental and biological samples. Various techniques have been used to remove metal ions from aqueous solution [4-7]. Among related techniques, adsorption is considered to be the most promising process due to its easy handling, high efficiency, selectivity and also the availability of different adsorbents [8,9]. Therefore, the effort has been made to design and prepare new sorbent functional polymers containing specific functional groups, such as, amino, hydroxyl, carboxyl, tetrazole, triazine, thiol, thizole and amidoxime, to form strong complexes with metal ions in aqueous media [10-14]. Among functionalized polymers, those with functional groups including nitrogen donor atoms have attracted much attention. These groups can be graft onto the backbone of polymer chains and apply for the removal of metal ions from aqueous solution, but with low metal sorption capacity [15-18]. Thus, we attempted to prepare new chelating polymer materials containing amino ligands, with high sorption capacity, high rate of sorption and low cost of sorbent with better analytical parameters in comparison with the similar samples [19-23]. Polyacrylonitrile(PAN) can be a suitable material for environmental applications, because it is common commercial product and an inexpensive. So, cross linked resins (PAN derivatives) can be applied in the clean technology methods for the adsorption of toxic metal ions. Melamine, which has three aromatic nitrogen atoms and three free amino groups in its molecule has a great potential to adsorb metal ions [24,25]. Recently, the synthesis of chelating resins containing melamine ligands have been used for the removal of metal ions such as Zinc, copper, and lead, but with low metal adsorption capacity and rate [26-28]. The

Chemical modification of PAN with chelating agents such as melamine may produce adsorbent with the high hydrophilicity required for the fast kinetics of metal ions uptake and high adsorption capacity without to be used additional expensive additives.

In this study, first cross-linked resin was prepared by the reaction of PAN and hydrazine hydrate as a cross-linking agent via nucleophilic addition reaction. The resin was modified with melamine as a grafting agent by direct reaction of a primary amine group of melamine with nitrile functions in pendant groups of cross-linked polymer to obtain new chelating resin. The adsorption performance of resulting resin was investigated in aqueous solutions for various metal ions such as Cu (II), Zn (II), Pb (II) .

2. EXPERIMENTAL

2.1 Materials and instruments

The monomer, acrylonitrile (Merck, Germany) was distilled under normal pressure and stored in refrigerator. Hydrazine hydrate (80%) was purchased from (Merck, Germany), Copper (II) nitrate [$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$], lead (II) nitrate [$\text{Pb}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and zinc (II) nitrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] were provided from Fluka and used without further purification. Organic solvents and other chemicals such as dimethylformamide (DMF), ethanol, methanol, benzoylperoxide and melamine were purchased from Merck or Aldrich and used without further purification.

The IR spectra were recorded in the region 4000-400 cm^{-1} on a Bruker TENSOR27 FT-IR spectrometer (Germany) by preparing KBr pellets. The metal absorption capacity of polymer was measured by an AA-670 Shimadzu atomic absorption spectrometer (Japan) and ANA77 (UV-Vis) spectrophotometer (Japan) at room temperature in aqueous solution. Elemental analysis of the polymer was carried out using a EURO EA 3000(Italy).The gel permeation

chromatography (GPC) measurements were conducted at 25°C with a Agilent1100 instrument

2.2. Cross-linking of polyacrylonitrile (CPAN)

PAN was prepared by the free-radical polymerization of acrylonitrile at 70°C with benzoyl peroxide as initiator [29]. For synthesis of the Cross-linked polymer, 0.5 g of polyacrylonitrile (PAN) and 40 mL of H₂O and

10ml of hydrazine hydrate (80%) were added into a 100 mL flask with refluxing for 6 h at 100°C. After the reaction, the obtained resin was filtered, washed with distilled water until the filtration became neutral, and then washed thoroughly with ethanol and dried at 80°C in vacuum oven overnight. The cross-linking degree was calculated as follows (Eq. 1):

$$\text{The Crosslinking degree} = \frac{\text{Crosslinking polymer quality} - \text{The initial polymer quality}}{\text{The initial polymer quality}} \times 100 \quad (1)$$

2.3. Preparation of CPAN-M

To a 100-mL three-necked flask 0.5 g of cross-linked PAN and 30 mL of DMF were added under stirring for 10 min. The flask was then placed into an oil bath and heated to 100 °C, and 1.2 g (9.5mmol) of melamine was immediately added. The reaction mixture was refluxed under stirring for 10 h. The obtained resin was filtered, washed with distilled water, and ethanol several times and dried at 70°C in vacuum overnight. The yield of reaction was 81%.

2.4. Adsorption studies

The batch sorption tests was carried out to study the sorption performances of Cu (II), Pb(II) and Zn(II) on chelating resin. The CPAN-M (0.05 g) was stirred with excess metal salt (100 mgL⁻¹) at a room temperature of 25°C. In addition, the desired pH was adjusted to 2, 3, 5 and 7 by adding moderate 0.01 M HCl or NaOH. The kinetics of metal ions absorption was carried out by taking 0.05 g CPAN-M and 30 mL of 100 mg L⁻¹ metal ion concentration. The chelating resin sorption rate was carried out by shaking the mixture of adsorbent (0.050 g) and metal ions solution (30ml L, 100mgL⁻¹, pH 5.0) at

different time intervals at 25°C. The mixtures was vibrated for 3 h to ensure that the sorption process reached complete equilibrium and the residual amount of metal ions were collected to determine the final ion concentration by AAS or UV-Vis spectrophotometer. The adsorption capacities, (mg g⁻¹) of resins in various conditions were calculated as follows (Eq. 2):

$$q = \frac{(C_0 - C_f) \times V}{W} \quad (2)$$

where q is the adsorption capacity (mg g⁻¹), C₀ and C_f are the initial and final concentrations (mgL⁻¹) of metal ion in the aqueous solution, respectively, V is the volume of metal ion solution (L) and W is the weight of modified resin (0.05 g).

2.5 Desorption of metal ions in acidic medium

The metal ions loaded polymer immersed in HCl (1M) solution (PH=5) with a magnetic stirrer at 25 °C for 1h. After that, the mixture was filtered and the final metal ion concentrations in the solution were determined by UV-vis spectrophotometer. The desorption ratio (D %) was calculated as follows (Eq. 3) :

$$D\% = \frac{\text{mmoles of metal ion desorbed to the HCl solution}}{\text{mmoles of metal ions desorbed on to polymer}} \times 100 \quad (3)$$

2.6. Adsorption selectivity

The adsorption selectivity of the CPAN-M was investigated under competitive conditions, and approximately 0.05 g of the obtained resin was placed

in contact with 50 mL of a binary mixture and ternary mixture (pH 5.0) in which the concentration of Cu(II), Zn(II) or Pb(II) ions was 100mgL⁻¹. The mixture was shaken for 3 h at 25 °C.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of the CPAN-M resin

In this study, polyacrylonitrile was prepared by free radical polymerization with benzoyl peroxide as initiator by the method considered in ref [29] (yield:83%). The number and weight average molar masses (M_n and M_w) of this polymer determined by GPC were 0.221×10^5 and 0.255×10^5 g/mol, respectively, with distribution index of 1.16.

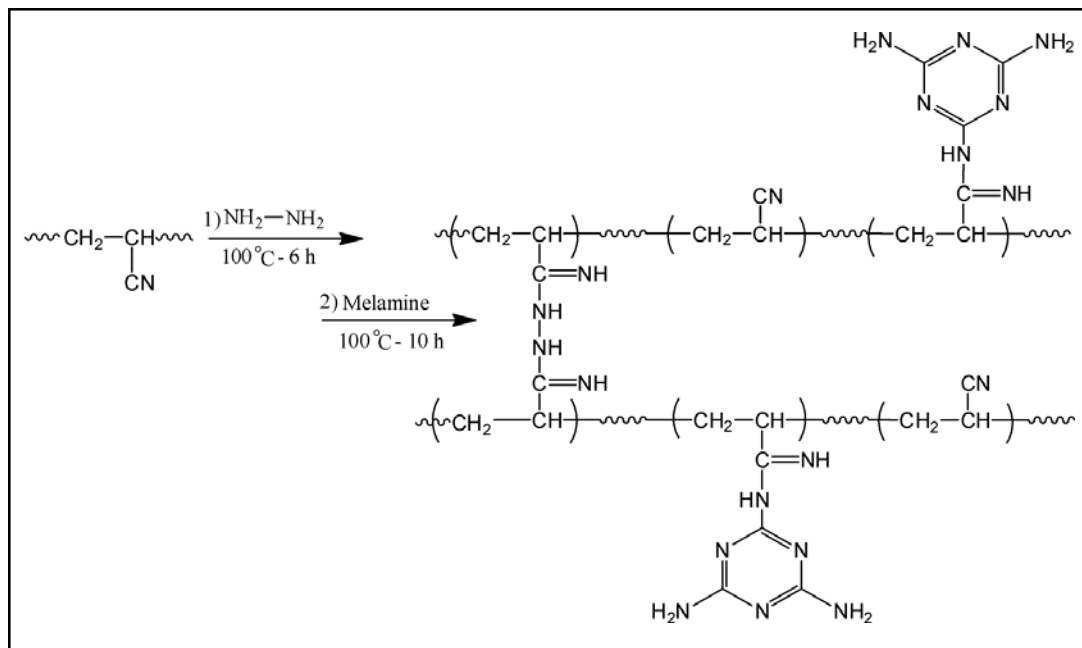
In the process of CPAN-M preparation (scheme 1), various organic solvents used would dissolve PAN, so it is essential to prevent PAN from dissolving in water and organic solution. Hydrazine hydrate is often selected as crosslinking agent to cross PAN to keep its

fibrous property in the first step. The prepared resin was found to be insoluble in common organic solvents and water, suggesting the formation of a cross-linking structure. The resulting crosslinking degree of CPAN was estimated to be 11% by the weight method.

In the second step, CPAN-M was synthesized with the reaction of nitrile moieties of the PAN polymer. The amine group of melamine reacted with nitrile repeating groups in the CPAN polymer backbone to form chelating resin bearing amidine linkage and amine groups.

The percentage conversion of nitrile group on the surface the modified CPAN fiber is calculated from follow equation [30]:

$$C = \frac{(W_1 - W_0)}{W_0} \times \frac{53}{126} \times 100 \quad (4)$$



Scheme 1. Synthesis of CPAN-M

Where C (%) is the conversion of nitrile group in the CPAN, W_0 is the weight of the CPAN fiber, W_1 is the weight of the CPAN-M fiber, 53 and 126 are the molecular weights of acrylonitrile monomer and melamine, respectively.

Table 1 shows the effects of the reaction conditions on the conversion of nitrile group in CPAN. As shown in Table 1, the conversion of the nitrile group in the CPAN increased along

with the increase of concentration of melamine in resulting mixture. The conversion depends on the amount of melamine molecule diffused from the reaction solution into the CPAN resin. The increasing melamine dose as grafting agent and reaction time effectively promoted the molecular diffusion of melamine into the CPAN and increased the reaction probability between amino and the nitrile groups.

TABLE 1. Effects of the reaction conditions on conversion of nitrile groups in CPAN resin dose: 0.50 g, temperature: 100 °C

No.	Time(h)	melamine dose (mmol)	Conversion%
1	3	9.5	33
2	6	9.5	52
3	10	9.5	59
4	10	3	21
5	10	6	46
6	10	12	59

FT-IR spectra of PAN, CPAN, and CPAN-M (Figure1), showed the absorption at about 1650 cm^{-1} and 3500 cm^{-1} assigned to stretching vibration of C=N and O-H due to the presence of water, respectively. The comparison of PAN, CPAN and CPAN-M spectra reveals that the intensity of C=N stretching vibration in PAN became weaker in CPAN because of cross linking of PAN and further decreased in CPAN-M.

The spectra of the CPAN-M fiber showed new absorption bands at 1659 cm^{-1} and 1554 cm^{-1} and 3334 cm^{-1} . These can be assigned to the stretching vibrations of the amidine group (N-C=N), the C=N stretch of the triazine ring and

the primary amine (NH_2), respectively [27, 31].

The results of elemental analysis of PAN, CPAN and CPAN-M are shown in Table 2. It was found that N/C ratio of CPAN was higher than that of PAN because of the presence of hydrazine into CPAN, while N/C ratio of CPAN-M was significantly higher than that of CPAN, suggesting that nitrile group in CPAN was reacted with hydrazine as grafting agent leading to the increase of nitrogen content. Therefore, it could be concluded from FT-IR spectrum and elemental analysis that a number of the nitrile groups are converted to amidine groups and the grafting reaction was efficient.

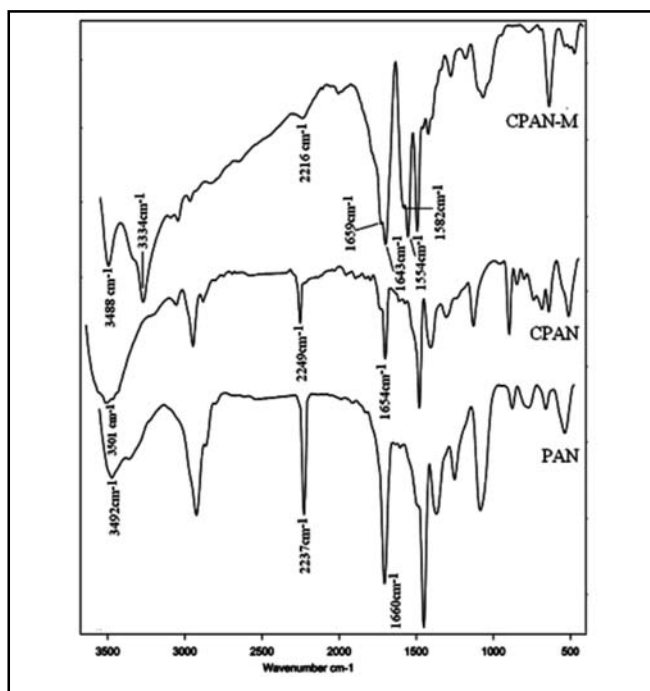


Figure 1. FT-IR spectra of: PAN, CPAN and CPAN-M

3.2. Effect of experimental conditions on adsorption process

3.2.1 Effect of pH

The initial solution pH plays an important role in metal ions adsorption from aqueous solutions, which is related to both the speciation and solubility of metal ions and the dissociation degree of functional groups from adsorbent surface.

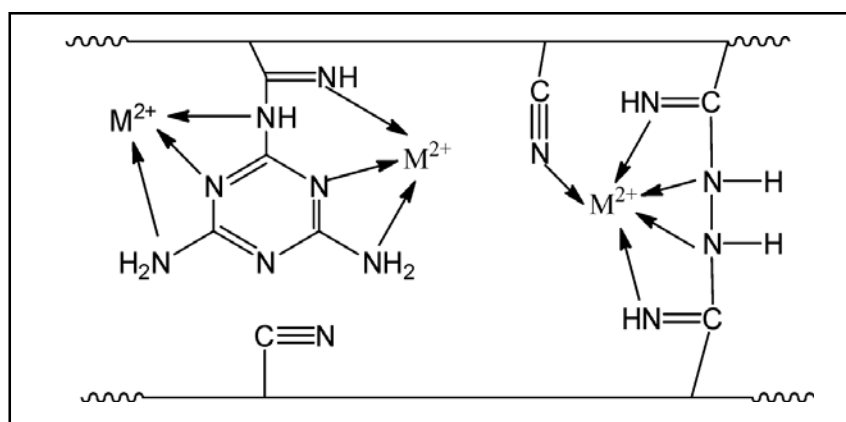
Figure 2 shows adsorption capacities and the effect of pH values ranging from 2 to 7 on the removal of Cu (II), Pb(II) and Zn(II) by the CPAN-M resin. It can be seen from figure 1 that the sorption of all three metal ions increases as the pH increases to reach at an equilibrium pH of around 5. The sorption of metal ions at pH values below 3 is low. At low pH, the protonation of the primary amines of the melamine ligands giving a strong electrostatic repulsive force to

TABLE 2. Elemental Analysis of PAN, CPAN, and CPAN-M

Sample	N%	C%	H%	N(mol) C (mol)
PAN	24.94	66.38	5.49	0.322
CPAN	28.19	62.54	5.67	0.386
CPAN-M	47.67	44.11	4.88	0.926

the positively-charged selected metal ions could thus explain this weak adsorption process [32]. At higher pH values (higher than 3), the nitrogen of primary amine group in the side chain of the resin formed a completely deprotonated form, so the metal ions uptake was intense and the reactive sites could be occupied with metal ions (scheme 2). At pH

values higher than 5, the removal efficiency value of all three metal ions is approximately constant and adsorption process occurs simultaneously with the precipitation of metal hydroxide, thus, to avoid the precipitation of selected metal ions, no adsorption experiments were done at a pH value higher than 7.



Scheme 2. Adsorption mechanism of CPAN-M for metal ions

As it is clear from Figure 2, the adsorption capacity of metal ions for obtained resin is in the order as follow: Cu (II) > Zn (II) > Pb(II). The Cu (II) ion adsorption capacity of resulting resin

was higher than the other metal ions. The Cu (II) is smaller ionic radius, thus, it can enter into the pores of prepared resin easier than the other ions.

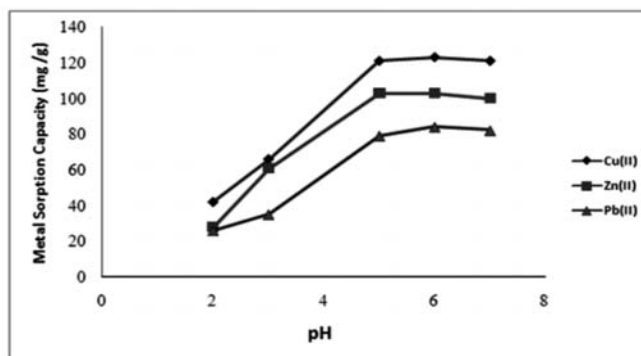


Figure 2. Effect of pH on the sorption of single metal ions (Cu(II), Zn(II) and Pb(II)) onto, CPAN-M, initial metal concentration 100 mg/L of each resin (30 ml).

3.2.2. Adsorption Kinetics

The effects of different adsorption times on the CPAN-M adsorption capacity toward selected metal ions are shown in Figure 3. As evident in the figure, metal ions adsorption capacity of the resin increased significantly with increasing time during the initial stage and then decreased slowly, followed by a continuous increase at time. The results showed that contact time of 20 min was enough for complete sorption of

metal ions from aqueous solution. The adsorption of metal ions onto the CPAN-M involves the following steps. First, the metal ion adsorb onto the surface of the resin, where it reacts with active sites of resin, thus accelerating the adsorption process rate. Second, the metal ion diffuses into micro porous resin, decreasing the adsorption rate. Finally, adsorption equilibrium is achieved.

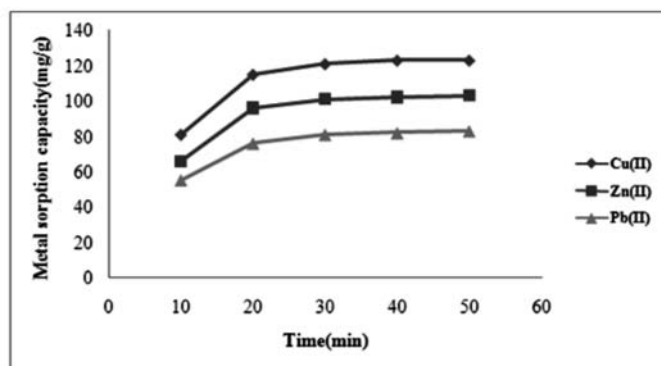


Figure 3. Effect of contact time on metal ion adsorption onto on to CPAN-M adsorbent: 0.05 g, V: 30 mL, Temp.: 25°C, pH: 5

The pseudo-first-order and pseudo-second-order kinetic models have been showed the sorption mechanisms of CPAN-M and calculated as follows equations: [33, 34]:

$$\log (q_e - q_t) = \log q_e - (k_1 t / 2.303) \quad (3)$$

$$t/q_t = 1/k_2 q_e^2 + \frac{t}{q_e} \quad (4)$$

Where q_t and q_e (mg g^{-1}) are the adsorption amount at given time t and equilibrium time, respectively. k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the pseudo-first-order and the pseudo-second-order constant, respectively. The kinetics results obtained from the plots for sorption of metal ions onto CPAN-M are shown

in Table 3. The pseudo-second-order kinetic values are in good agreement with experimental data of the removal of all three metal ions by the resin according to the correlation coefficients (R^2) of the linear plots.

3.2.3. Adsorption isotherm

The effect of initial concentration on metal ions removal is investigated at different concentrations (10 to 80 mg L^{-1}), keeping all other parameters constant, as shown in Figure 4. The adsorption capacity of selected metal ions by the CPAN-M resin was increased with the increase in initial metal concentration up to 20 ppm for Cu (II) and Zn (II) and 40 ppm for

TABLE 3. Kinetics of metal ions sorption onto CPAN-M

Elements	Pseudo-first order model			Pseudo-second order model		
	q_e (mgg ⁻¹)	k_1 (min ⁻¹)	R^2	q_e (mgg ⁻¹)	k_2 (gmg ⁻¹ min ⁻¹)	R^2
Cu(II)	38.01	0.071	0.800	142.8	1.44×10^{-3}	0.995
Zn(II)	33.11	0.069	0.799	125	1.45×10^{-3}	0.994
Pb(II)	28.05	0.062	0.871	90.90	2.20×10^{-3}	0.996

Pb(II). This can be explained with the high concentration of metal ions and this driving force for mass transfer [35]. Reduction in the amount of adsorption capacity was accompanied by further increase in the phenomenon may be due to saturation of active sites of the resin with the metal ions at higher concentrations.

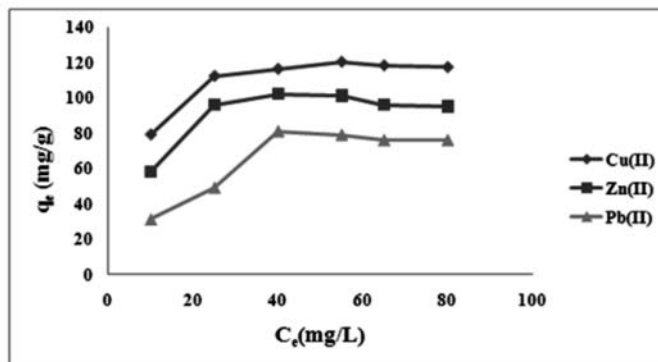


Figure 4. Effect of concentration on metal ion adsorption onto CPAN-M
Adsorbent : 0.05 g, V: 30 mL, Temp.: 25°C, pH: 5

Adsorption isotherms of selected metal ions by CPAN-M are obtained at optimum pH value for each metal ion as shown in table 4.

The Langmuir and Freundlich isotherm models are described as the following equations, respectively [36, 37]:

$$1/q_e = (1/q_m b C_e) + 1/q_m \quad (5)$$

$$\ln q_e = \ln K_f + (1/n) \ln C_e \quad (6)$$

where C_e (mg L⁻¹) is the equilibrium metal ions concentration, q_m (mg g⁻¹) is the maximum

sorption capacity of CSMA-HPC, b (L mg⁻¹) is Langmuir constant that indicates the heat of sorption, K_f (mg¹⁻ⁿ Lⁿ g⁻¹) and n are the Freundlich constant related to the sorption capacity and sorption at equilibrium concentration respectively.

By comparing the R^2 values for the applied Langmuir and Freundlich models, we can see that the Langmuir isotherm fit the experimental data better than the Freundlich equation for the adsorption of selected metal ions at room temperature. This indicates that the surface of

TABLE 4. Adsorption isotherm parameters for the sorption of metal ions onto CPAN-M

Elements	Langmuir isotherm			Freundlich isotherm		
	q_m (mgg ⁻¹)	b (Lmg ⁻¹)	R^2	K_f (mg ¹⁻ⁿ L ⁿ g ⁻¹)	n	R^2
Cu(II)	142.85	0.134	0.984	50.11	4.65	0.893
Zn(II)	124	0.091	0.954	34.67	3.73	0.806
Pb(II)	125	0.032	0.968	9.84	1.93	0.921

the resulting resin was made up of homogeneous sorption patches with all the adsorption sites having equal adsorbate tendency and monolayer surface coverage of CPAN-M is the main sorption mechanism based on assumption of Langmuir model.

3.2.4. Desorption study

Desorption of selected metal ions was administered by 1 M HCl solution. The CPAN-M resin which was loaded by the maximum amounts of the respective metal ions in optimum pH, was immersed in 1M HCl and the solution was shaken until equilibrium was reached (60min). After filtration, the final concentrations of metal ions in the aqueous solution were estimated by UV-Vis spectroscopy. The results were summarized in table 5. The results indicate that all metal ions have desorption ratio up to 89%.

TABLE 5. Percent of desorption for single metal ions

Polymer	Percent of desorption		
	Cu(II)	Zn(II)	Pb(II)
CPAN-M	95.3	92.6	89.9

3.3. Thermogravimetric Analysis

Thermal gravimetry analysis CPAN-M and its copper complex curves (prepared at pH 5) are shown in Figure 5. Thermogravimetric analysis

indicates that obtained resin decomposed with three steps at 100–200°C, 220–345°C and 410–600 °C respectively. In this polymer, the first decomposition step at a temperature about 165 °C can be attributed to the loss of water moistures. The second and last stage of weight loss can be attributed to decomposition of modifying and crosslinking agents. The weight loss pattern of CPAN-M and its complex up to about 240°C was approximately the same, but between 250°C and 600°C polymer was decomposed stronger than the polymer-Cu complex. There remained mass polymer-Cu complex (29 wt %) at 600 °C corresponds to the formation of copper oxide.

3.4. Comparison with Other Adsorbents

The comparative experiments on adsorption of Cu (II), Pb (II) and Zn(II) with those of other published results is given in Table 6. The comparative results indicate that the removal efficiencies of the prepared resin and higher or comparable, in some cases, than that of common presented adsorbents.

3.5. Adsorption selectivity

The adsorption selectivity is an important factor for evaluating the properties of an adsorbent.

The competitive adsorption among C(II), Zn(II) or Pb(II) was examined in a binary mixture and ternary mixture. As shown in Table 7, in a binary

TABLE 6. Comparison of the maximum adsorption capacities of selected metal ions among different adsorbents

Adsorbents	Cu(II)	Zn(II)	Pb(II)	Ref
PAN-g-CS	-	2.10	12.93	[19]
APAN nanofiber mats	24	-	14	[20]
D-PAN	-	-	144	[21]
Amidoxime-functionalized polyacrylonitrile	105	91	345	[22]
P-Polyacrylonitrile nanofiber	-	-	98	[23]
CPAN-M	123	103	84	This study

system the presence of Zn(II) and Pb(II) had little effect on the adsorption of Cu(II) by CPAN-M, whereas lead ion adsorption was interfered to a great extent in the presence of Cu(II) or Zn(II). This phenomenon can be explained based on the HSAB theory [38]. Based on the obtained results, the triazine and the amine groups on the obtained resin have the properties of a soft base. Among heavy metal ions, copper ion is well-known soft acids and has higher polarizability. However, zinc and lead being borderline acids that have less affinity to soft bases compared to strong soft acids [39].

Therefore, CPAN-M resin prefers adsorbing Cu (II) rather than Pb (II) and Zn (II) ions.

When three metal ions are present, CPAN-M adsorbs the selected metal ions in the following order: Cu(II) > Zn(II) > Pb(II). This affinity order was the same as that in the single metal ions adsorption studies.

4. CONCLUSION

The novel modified polyacrylonitrile (PAN) fiber have been successfully synthesized by the reaction of the polymer by hydrazine hydrate as cross-linking agent and melamine as

TABLE 7. Competitive adsorption among Cu (II), Zn (II) and Pb (II) in binary and ternary mixtures (metal ions initial concentration 100 mg/L, pH=5).

Metal ions mixture	Removal percentage		
	Pb(ii)	Zn(II)	Cu(II)
Pb(II)	39.4	58.8	-
Pb(II)	31.6	-	79.2
Zn(II)	-	52.3	74.4
Pb(II)- Zn(II)-Cu(II)	25.4	44.5	73.4

grafting agent. This resin (PAN) was used for the adsorption of Zn(II), Cu (II) and Pb (II) from aqueous solutions. The results suggest that the adsorption process is affected by solution

pH, contact time and initial concentration of the metal ions. The adsorption of selected metal ions is found to be effective in the pH range of 3–6 by the obtained polymer. The adsorption

rate of CPAN-M resin was fast and the largest fraction of the adsorbed metal ion was obtained within 20 min. The absorption behaviour were better described by the Langmuir isotherm model based on its correlation coefficient values and adsorption kinetics fits well with the pseudo second-order rate equation with rapid initial adsorption rate. The prepared resin is reusable adsorbent for the highly efficient sorption of selected metal ions.

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