Removal of Cu^{+2}, Zn^{+2} and Cd^{+2} from Aqueous Solution by Using Ion Exchanger Derived from Sack Polypropylene Grafted with Maleic Acid and its Derivatives

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ABSTRACT

Grafting of wastes polypropylene taken from sack with some active functional groups like maleic anhydride, N- phenylmaleamic acid, N(o-chloro-phenyl) maleamic acid, N(2,6-diethyphenyl) maleamic acid and N(3-chloro-4-methylphenyl) maleamic acid were accomplished via free radical polymerization.

The grafted polymers were examined as an ion exchanger toward Cu^{+2}, Zn^{+2} and Cd^{+2} ions from their aqueous solutions. The initial concentrations of metal ion solution, pH of the extraction medium and treatment time were studied as a factors influence the efficiency of extraction. The r esults were constructed with some isotherm models (Langmuir, Frendlich and Dubiuin-Radushkevish models). The langmuir and Dubini-Radushkevish isotherm are the more suitable models to describe the results than Frendlich model.

Keywords: ion exchanger, polypropylene, maleic anhydride, maleamic acid.

$$Cd^{+2} \quad Zn^{+2} \quad Cu^{+2}$$

$-$ N $Cd^{+2} \quad Zn^{+2} \quad Cu^{+2}$

($-$ $-$ $-$ 6,2) N   ($-$ $-$) N

.   ($-$ $-$4$-$ $-$3)N

                    $Cu^{+2} \quad Zn^{+2} \quad Cu^{+2}$

        (pH)

. $-$. $-$

INTRODUCTION

Polypropylene (pp) is a versatile material of several uses because of its low density, low cost, easy processing and ability to be modified. Growing production of pp material in modern society create a large problem of leaving a lot of tons of pp discharged as a west to the environment.On the other side increasing level of metal ions in west and industrial water represents a serious risk to human health and environmental system (Wlan *et al*., 2008 and Sarang *et al*., 2007). One of the proposal methods to overcome these problems is the using of the modified pp as a chemisorption material in polluted waters (Ji *et al*., 2011 and Artemento *et al*., 2003).

Various methods have been used to modify pp in order to improve its efficiency as an ion exchanger. Chemical modification is one of the main directions of the development in modern ion exchanger (Gupla *et al*., 2008). In a related work a solid phase extractors have been prepared by the function of organic chelating agents such as maleic anhydride on to polyethylene to get high efficiency of extraction metal ions from its aqueous solutions (Khattab and Ismail, 2010). The grafting of acrylic acid on pp was carried out for preparing a weak ion exchanger to remove the copper ions in aqueous solution.

Grafting of acrylonitrile onto pp fiber followed by amination with diethylene triamine will produce a high adsorption capacity ion exchanger for mercury ions (Ma *et al*., 2009). It was noticed that the amination of pp fiber will produce a weak-base anion exchanger membrane (Joo-Hee Hong, 2011).

In the present work we investigate the performance properties of the wasted pp (which was left from sacks) as an ion exchanger after some modifications. The improvements include grafting pp with maleic anhydride and four types of maleamic acids in order to get some chelation with metal ions.

EXPERIMENTAL

Materials

The sack pp was cleaned and catted to 1×1 cm dimension and used as source of pp. The catalyst Luperox-F (Donjeen) was used as a commercial product. All the solvents and reagents were used as received.

Preparation of maleamic acids

In a conical flask, 10 g of maleic anhydride was dissolved in dry chloroform, 12 ml of aniline or equivalent amount of its derivatives(3-chloro 4- methyle aniline, 2, 6- dimethyle aniline and o- chloroaniline) was added drop wise with stirring under temperature below 10∘C. The precipitated maleamic acid was filtered, recrystallized from ethanol and dried under vacuum.

Grafting reactions
Grafting of pp with maleic anhydride (MAn)

The reaction was carried out in a three necked flask equipped with nitrogen inlet, thermometer, reflux condenser, 2g of pp was dissolved in 20 ml of 1,2-dichlorobenzene at the boiling point of the solvent, certain amount of MAn and half amount of the initiator were added and bubbled for 5 min. with nitrogen gas. The reaction was carried on for 24 hr. The remain half amount of the initiator was then added and the reaction was continued for

another 24 hr. The polymeric product was precipitated from acetone, filtered, washed with acetone and dried under vacuum at 50∘C.

Grafting of pp with maleamic acids

The grafting reaction of maleic anhydride onto pp was repeated with maleamic acids except that the reaction time is carried out for 1 hr and the initiator is added one time.

Grafting of maleamic acids onto pp grafted previously with Man

The samples of MAn grafted onto pp was grafted with different ratios of maleamic acids using the same procedure of grafting maleamic acids onto pp.

Evaluation of grafting degree

The degree of grafting of pp with MAn was determined by titrating the acid groups with alcoholic KOH according to the published work (Khattab and Ismail, 2010).

The amount of maleamic acids grafted onto pp was determined spectrophotometrically as follows :

After precipitating the polymaleamic acid from the filtrate solution that produced from grafting reaction, 0.2 ml of this solution was added to 5 ml of toluene, the absorbance of the formed complex was measured at 320 nm. The amount of the maleamic acid was calculated from the calibration curve between the absorbance and the maleamic acid concentrations. The grafted amount can be calculated from the equation:

$$\% \text{ Grafting} = \frac{(C+B)-A}{m}$$

Where A represent the weight of the maleamic acid added to the reaction, B is the amount of the unreacted maleamic acid, C is the weight of the polymaleamic acid and m is the weight of pp.

Extraction efficiency

Samples of the highest degree of grafting with MAn and with maleamic acids and the samples with mixed grafting have been chosen to study as an ion exchangers toward the metal ions Zn^{+2}, Cu^{+2} and Cd^{+2} by using batch system technique. The concentration of the metal ions in their solutions were determined before and after treatment by atomic absorption spectrophotometer type Pye Unicam SP9. The studied factors which affecting the efficiency of extraction are the concentration of metal ion solutions, pH of the medium and time of treatment.
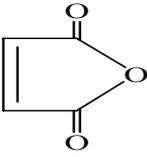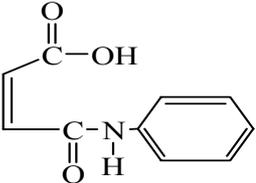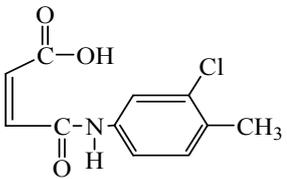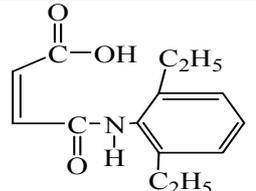
The regeneration efficiency of the adsorbed metal ions was studied by treating the loaded polymers with different concentration of hydrochloric acid in an electrical shaker for a period of time equal to 4 hrs. The experimental data have been treated theoretically by fitting to the isotherm models of Langmuir, Freundlich and Dubinin-Radushkevich in order to explain the nature of adsorption process via extraction the ions from their solutions.

RESULTS AND DISCUSSION

The prepared reactive species are listed in Table (1). MAn and maleamic acids can be inserted to the pp chain randomly as a single functional groups through their unsaturated moieties. The grafting reactions were carried out through free radical polymerization process in the presence of the initiator 1,4-di(2-tert-butyl peroxy isopropyl benzene) (Luperox –F).

The infrared spectrum of the grafted polymers confirm the presence of the specific functional groups related to the grafted moieties onto pp chains. The IR. Spectra of MAn grafted pp shows two peaks at 1711 cm^{-1} and at 1730 cm^{-1} which are characteristic of cyclic anhydride. In the spectra of N-phenyylmaleamic acid graft pp another four peaks appeared in between (1450-1599) cm^{-1} which are related to C=C group of the aromatic ring, as well as the specific two amides bands at 1697 cm^{-1} and 3211 cm^{-1}, mean while the absorption peak at 1720 cm^{-1} was related to the carbonyl group of the acid moiety.

Table 1 : Chemical structure of the prepared maleamic acids.

Maleamic	Maleamic acid symbol	Structure	Colour	m.p / C°
Maleic anhydrid	AMN		White	54
N-phenyl maleamic acid	PMA		White	206-208
N-(3-chloro-4-methylphenyl) maleamic acid	CMPMA		Green	193-194
N-(2,6-diethylphenyl)maleamic acid	EPMA		White	148-149.5
N-(o-chlorophenyl) maleamic acid	CPMA		White	132-133
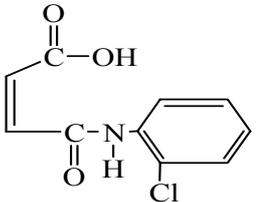
The spectra of the derivatives N-phenylmaleamic acid graft pp show another bands refer to C-Cl appeared in about 720 cm^{-1}, where by the spectra of the MAn and maleamic acid graft pp indicates the presence of the two moieties grafted onto pp. The figures show a multiple peaks accumulate at about 1720 cm^{-1} related to the different carbonyl groups belong to the grafted moieties (amide, carboxylic acid and anhydride). Table (2) shows the percentages of the grafted units onto pp. The data indicates that the grafted ratio was effected by the feed ratio and the percentage of the initiator. The DSC curves of the grafted polymers obtained on heating are shown in Fig. (1). Table (3) shows the thermal stability

characteristic, the crystalline temperature T_C , the crystalline melting T_{cm} and two curing temperatures obtained from DSC thermogram.

Table 2: percentage of active group grafted to pp.

No.	Reaction time/ hr.	% Initiator	MAn% feed		MAn % grafted
			MAn		
1	48	3.6	10		2.744
2	48	4.8	10		7.02
3	48	9.6	15		8.53
4	48	9.6	30		10.5
5	48	9.6	50		18.14
6	48	9.6	75		19.623

No.	Reaction time/ hr.	% Initiator	CMPMA % feed		CMPMA % grafted
			CMPMA		
7	1	2	10		0.5
8	1	2	20		19.5
9	1	2	50		54

No.	Reaction time/ hr.	% Initiator	CPMA % feed		CPMA % grafted
			CPMA		
10	1	2	10		0.06
11	1	2	20		16
12	1	2	50		53.3

No.	Reaction time/ hr.	% Initiator	% DEPMA feed		% DEPMA grafted
			DEPMA		
13	1	2	10		0.7
14	1	2	20		10
15	1	2	50		10

No.	Reaction time/ hr.	% Initiator	% PMA feed		% PMA grafted
			PMA		
16	1	2	48		36.2
17	1	2	58		52.7

No.	Reaction time/ hr.	% Initiator	% CPMA feed	% Man grafted	%CPMA grafted
			CPMA and MAn		
18	1	2	5	18.14	49.9
19	1	2	17	8.5	15.39
20	1	2	59	2.7	49.9

No.	Reaction time/ hr.	% Initiator	%CMPMA feed	% MAn grafted	% CMPMA grafted
			MAn and CMPMA		
21	1	2	5	18.14	4
22	1	2	17	8.5	10
23	1	2	59	2.7	54.15

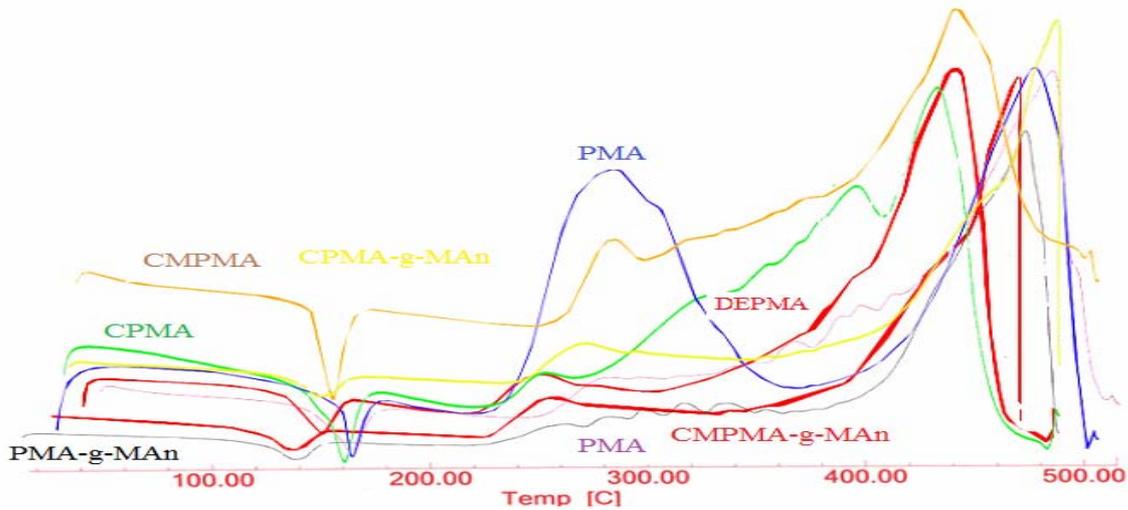| No.	Reaction time/ hr.	% Initiator	% PMA feed	% MAn grafted	% PMA grafted
			MAn and PMA		
24	1	2	5	18.14	1.05
25	1	2	17	8.5	10.2
26	1	2	59	2.7	27.9

Fig. 1: DSC –Thermogram of the grafted polymer

Table 3: DSC thermal parameters of the grafted polymers.

Grafted moiety to pp	$T_C / C°$	$T_{cm} / C°$	1st Curing Temp./ C°	2nd Curing Temp./ C°
MAn	160	233	274	459
DEPMA	162	235	265	445
CAPMA	163	250	290	433
CPMA	159	240	394	431
PMA	163	265	---------	460
MAn PMA	150	260	---------	478
MAn + CMPMA	147	250	---------	489
MAn CPMA	164	---------	---------	487

Extraction efficiency

The samples number (5, 9, 12, 15, 17, 20, 23, 26) have been chosen to study as an ion exchangers toward Cu^{+2}, Zn^{+2}, Cd^{+2} metal ions, whereby they have a maximum grafting percent of the active species. Limited volumes of metal ions solutions were shaken with a known weight of the resin for 24 hr. The amount of metal ion extracted (q_e) was calculated as (mg/g) by using the equation :

$$q_e = \frac{(C_o - C_e)\, v}{m}$$

where C_o and C_e (mg/L) are the concentrations of the metal ions initially and at equilibrium respectively. V is the volume of the solution (L), m is the polymer weight (g). The initial metal ion concentration, the pH of the medium and the time of treatment have been studied as a factors effected the efficiency of extraction.

Effect of metal ion concentration

The loading capacities (q$_e$) of the investigated copolymers from different concentrations of metal ions solutions are shown in Table (4). It is generally noticed that the efficiency of extraction was increased by the dilution of metal ions solutions. The acceptable explanation is that the diffusion of metal ion through the polymer folded chain will be more easy as the dilution increase. The results show that chelation efficiency have the following sequence with respect to some exceptions:

$$Cu^{+2} > Zn^{+2} > Cd^{+2}$$

In comparison with the diameter of metal ions which follow the order

$$Cu^{+2} \,(0.72\ A\circ) > Zn^{+2}\,(0.74\ A\circ) > Cd^{+2}\,(0.97\ A\circ)$$

We can conclude that the efficiency of ion exchanging was proportionally increased by decreasing the volume of the metal ions (McGarvey, 2007). The results in Table (4) indicate that the type of the active functional group grafted to pp also will effect the efficiency of extraction. This factor is not clear and the result are too complicated to be explained, whereby the type of ion and the dilution factors have the major roll of efficiency. Anyway it was noticed that the extraction of copper ion is more efficient by maleamic acid units than by succinic group, while succinic unit will extract cadmium ion more efficient than the maleamic acid unit. The extraction efficiency of zinc ion seem to be similar with both cases of succinic or maleamic unit.

Table 4: Effect of ion solutions concentration S on qe of the different grafted pp.

polymer	(5)			(12)			(15)		
Ion \\ C$_o$ ppm	100	50	25	100	50	25	100	50	25
Cd^{+2}	76.7	60.8	165.7	76.7	60.3	165.2	94.9	60.8	145.2
Cu^{+2}	109.3	120.9	347.6	123.5	169.2	315.5	143.9	218.2	323.2
Zn^{+2}	108.9	60.2	336.4	78.6	23.1	30.2	78.6	60.2	336.1
	(17)			(9)					
	100	50	25	100	50	25			
Cd^{+2}	44.7	40.6	109.3	59.6	40.6	145.2			
Cu^{+2}	149.5	90.6	291.2	166.3	198.1	282.4			
Zn^{+2}	87.2	14.7	318.9	104.6	49.3	147.4			
polymer	(23)			(20)			(26)		
Ion	100	50	25	100	50	25	100	50	25
Cd^{+2}	63.7	52.5	137.1	51.73	54.6	145.2	65.6	60.8	16.1
Cu^{+2}	155.8	198.1	323.1	131.6	210.4	323.1	154.0	169.4	290.6
Zn^{+2}	57.03	87.4	30.1	72.5	60.2	267.11	35.4	15.8	30.1

Effect of pH

Sample number (12), which prepared from pp grafted by both CPMA and MAn, and sample number (20), which was grafted with o-chloro-N-phenylmaleamic acid only have been chosen to study the effect of pH of the medium on its extraction efficiency. Table (5) shows the load capacity of the polymer with the metal ions at different pH.

The results demonstrate that the largest amount of metal ion taken by the polymer was at normal pH or at pH7. There is a relative decrease in metal ion extracted by the resin as the pH is decreased or increased. The efficiency of the resin toward extraction of the metal ions at different pH was follows:

With polymer o-chloro-N-phenylmaleamic acid grafted onto pp:
$pH_2 = Cd^{+2} > Cu^{+2} > Zn^{+2}$
$pH_4 = Cd^{+2} > Zn^{+2} > Cu^{+2}$
normal solution $= Cu^{+2} > Zn^{+2} > Cd^{+2}$
$pH_7 = Cu^{+2} > Zn^{+2} > Cd^{+2}$
MAn + o-chloro-N-phenylmaleamic acid grafted onto pp
$pH_2 = Cd^{+2} > Zn^{+2} > Cu^{+2}$
$pH_4 = Zn^{+2} > Cd^{+2} > Cu^{+2}$
normal solution $= Cu^{+2} > Zn^{+2} > Cd^{+2}$

Table 5: Milligrams of extracted metal ions by 1g (qe) of polymer at different pHs. The initial concentration of the metal ions solution is 25 ppm.

Polymer (12)						
Ion \ pH	2	4	Normal solution*	7	9	10
Cu^{+2}	14.82	10.63	32.3	10.4	12.0	12.2
Zn^{+2}	12.7	15.6	30.1	-------	33.7	---------
Cd^{+2}	29.8	31.9	13.7	33.9	-------	---------
Polymer (20)						
Ion \ pH	2	4	Normal solution*	7	9	10
Cu^{+2}	22.2	80.6	31.5	10.4	12.3	12.26
Zn^{+2}	24.4	19.2	16.5	-------	--------	--------
Cd^{+2}	22.6	22.6	30.1	32.9	21.3	15.5

*

Ion	Cu^{+2}	Zn^{+2}	Cd^{+2}
pH	6.0	6.17	6.01

Effect of treatment time

The effect of time of treatment on the extractability at optimum working pH for the metal ions of the two chosen polymers are shown in Table (6). The results show that the extraction process reach equilibrium state at finite time, then there is a designating of the ions from the chelation with the polymers.

Table 6: Effect of time treatment on the q$_e$ of the polymers, the solution of the ions is at normal pH and at 25 ppm concentration.

Ion / Time	Polymer (12)				
	0.5 hr	1 hr	2 hr	4 hr	6 hr
Cu^{+2}	127.4	201.04	205.9	331.2	209.2
Zn^{+2}	74.2	98.1	193.2	156.7	86.4
Cd^{+2}	118.1	173.2	221.2	210.03	120.6

Ion / Time	Polymer (20)			
	1 hr	2 hr	4 hr	6 hr
Cu^{+2}	168.4	159.6	144.1	347.2
Zn^{+2}	331.8	303.1	273.7	---------
Cd^{+2}	567.1	108.9	77.5	92.4

Construction of isotherms and model fitting

Sorption isotherms were constructed by plotting the amount of metal sorbent (mg/g) against the equilibrium concentration of metal in solution (mg/L). The models that have been adopted in this study are the Langmuir, Freundich-Langmuir and Dubinin-Radushkevish equilibrium isotherm models.

Langmuir isotherm

This model was used to describe the adsorption on homogenous surface. The equation form can be represented as follows (Wany *et al.*, 2003):

$$q_e = \frac{Q_o K_L C_e}{1 + K_L C_e}$$

or on a linear form

$$\frac{C_e}{q_e} = \frac{C_e}{Q_o} + \frac{1}{K_L Q_o}$$

q$_e$ is the amount of the adsorbed metal in mg/g
K$_L$ (L/mg) is a constant relates to the heat of adsorption.
Qo the maximum adsorption capacity is the amount of metal ion at complete monolayer coverage (mg/g).

The linear plot of **C$_e$**/q$_e$ versus Ce gives the intercept value 1/K$_L$Q$_o$ and the slop 1/Q$_o$. the parameters Q$_o$ and K$_L$ are given in Table (7). It is clearly observed that the maximum adsorption of the metal ion in all type of the adsorption will follow the order:

$$Cu^{+2} > Cd^{+2} > Zn^{+2}$$
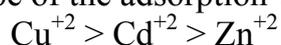
The poor ability of this model to represent the K$_L$ parameter is due to the fact that the Langmuir isotherm does not take into account adsorbate -adsorbate interaction (Quadjenia-Marouf *et al.*, 2010).

Freundlich isotherm

This model can be expressed as follow:

$$\text{Log } q_e = \text{Log } K_F + 1/n \ C_e$$

Where K_F and n are Freundlich constant represent the sorption capacity and the heterogeneity factor respectively (Hameed *et al.*, 2009). Our result did not fit with this equation, whereby the Freundlich model describe the adsorption on a heterogeneous site on solid surface. The isotherm is a weak Van der Weals type (Zhu *et al.*, 2008). This will give some explanation that the type of adsorption in the investigated polymers may have a chelation type.

Dubinin-Redushkevich (D-R)

This model can be used to describe adsorption on both homogeneous and heterogeneous surface (Zheng *et al.*, 2008; Shahwan and Erten, 2004). The linear form of this model can be expressed as:

$$\ln \ q_e = \ln q_{max} - \beta \ \varepsilon^2$$

Where q_{max} represent the total specific micropore volume of the sorbent. The value of β is related to the adsorption free energy, E (KJ/mol), which is defined as the free energy change required to transfer 1 mole of ions from solution to the solid surface (Dubinin *et al.*, 1947; Saltan *et al.*, 2007). (ε) is Polanyi potential, which can be described as :

$$\varepsilon = R \ T \ \ln (1 + 1/C_e)$$

R is the ideal gas constant (8.31 J/ mol.K) and T is the solution temperature (K). the value of E (KJ.mol) can be calculated from β value as follows:

$$E = \frac{1}{\sqrt{2\beta}}$$

The value of E(KJ/mol) gives information about type of adsorption mechanism as chemical ion-exchange or physical adsorption. The value of E between 8 and 16 KJ/mol correspond to chemical ion exchange process. In case of E<8 KJ/mol the mechanism is a physical sorption and if E is > 16 KJ/mol the partial diffusion is dominate (Erdem *et al.*, 2009, Ozcan *et al.*, 2006).

Table (7) indicate the calculation results of (D-R) equation parameters. The fitting of the experimental data on (D-R) equation indicate that this model is very suitable for describing the sorption of ions on the investigated polymers. The low values of E in all polymers indicates that the adsorption process of the studied metal ions follows physical adsorption.

Table 7: Isotherm constant estimated from Langmuir and D-R models.

Ion	Langmuir			D-R		
	Q_o/ mg/ g	R^2	q_{max} / mg/ L	β/ KJ/ mol	E/ KJ/ mol	R^2
Polymer (5)						
Cu^{+2}	108.9	0.9973	4.8	5.041	0.32	0.9944
Zn^{+2}	25.244	0.1	3.3	8.32	0.25	0.5112
Cd^{+2}	71.03	0.9573	4.13	4.6	0.33	0.9615
Polymer (12)						
Cu^{+2}	120.51	1	4.97	1.201	0.65	0.9097
Zn^{+2}	62.9	0.3254	3.8	4.7	0.33	0.7685
Cd^{+2}	70.6	0.9988	4.27	1.143	0.7	0.8255
Polymer (15)						
Cu^{+2}	137.912	0.9912	4.97	7.712	0.3	1
Zn^{+2}	33.831	0.1	3.1	8.8	0.24	0.5865
Cd^{+2}	91.93	0.998	4.6	1.99	0.502	0.7534
Polymer (17)						
Cu^{+2}	128.14	0.9613	4.8	3.3	0.4	0.8581
Zn^{+2}	25.244	0.1594	3.6	8.8	0.24	0.6695
Cd^{+2}	42.54	0.9818	3.7	5.1	0.313	0.9541
Polymer (9)						
Cu^{+2}	155.9	0.9972	1.63	2.022	0.5	0.8868
Zn^{+2}	99.2	0.5266	4.3	2.1	0.5	0.6392
Cd^{+2}	56.84	0.9901	4.10	1.33	0.5144	0.8236
Polymer (20)						
Cu^{+2}	149.43	0.993	5.196	5.62	0.3	0.9275
Zn^{+2}	37.4	0.4305	2.971	1.54	0.35	0.4305
Cd^{+2}	50.65	1	3.891	4.1	0.35	0.9979
Polymer (23)						
Cu^{+2}	125.8	0.987	5.1331	6.21323	0.3	0.6922
Zn^{+2}	55.95	0.6519	-----	-----	-----	0.1534
Cd^{+2}	57.3	0.9564	4.03	3.51	0.4	0.9128
Polymer (26)						
Cu^{+2}	137.14	0.9957	5.1	2.3	0.5	0.9887
Zn^{+2}	33.7	0.5561	----	----	----	0.2431
Cd^{+2}	59.8	0.9794	4.1	3.21	0.4	0.9749

Recovery efficiency

The adsorbate metal ions loaded on different adsorbent have been recovered by treating the loaded polymers with different concentration of eluent HCl. Table (8) shows the results of treating with 1N, 2N and 3N HCl for a period of 4hrs. The results shown that 2N concentration of HCl is the best one to give a higher efficiency for recovering the metal ions. The sequence of recover the metal ions is as follows with respect to some exceptions:

$$Zn^{+2} > Cd^{+2} > Cu^{+2}$$
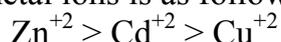
The regeneration efficiency of the adsorbent depends on the linkage force between the ions and the polymers. It is clearly observed that the linkage of metal ions with maleimic acid units are weaker than with MAn unit.

Table 8: Recovery percentage of metal ions from different adsorption by using different concentration of eluent HCl for a period 4 hrs at room temperature.

Ion \ Conc. HCl	5			12			15		
	1 N	2 N	3 N	1 N	2 N	3 N	1 N	2 N	3 N
Cu^{+2}	10.7	4.6	1.6	----	----	----	12.1	0.72	0.11
Zn^{+2}	14.74	6.67	5.7	54.9	>95%	23.23	20.6	>95%	>95%
Cd^{+2}	11.9	23.6	17.9	1.24	3.3	1.82	0.62	1.3	0.03

Ion \ Conc.	17			9			20		
	1 N	2 N	3 N	1 N	2 N	3 N	1 N	2 N	3 N
Cu^{+2}	2.6	10.4	0.3	5.5	2.9	6.1	3.3	2.813	2.4
Zn^{+2}	21.8	----	4.9	30.9	----	2.33	14.7	----	3.4
Cd^{+2}	0.8	2	0.423	5	0.24	0.1	7.7	5.44	1.7

Ion \ Conc.	23			26		
	1 N	2 N	3 N	1 N	2 N	3 N
Cu^{+2}	5.9	2.24	2.24	6.3	4.4	5.2
Zn^{+2}	6.89	----	----	35.2	----	6.8
Cd^{+2}	9.2	14.7	14.7	9.3	3.4	11.62

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