

Highly Efficient Chelating Polymers Based on Plastic Waste for Removal of Toxic Heavy Metal Pollutants

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NEW efficient chelating polymers CPs based on waste poly(methylmethacrylate) (PMMA) functionalized by itaconic acid moieties in absence and presence of montmorillonite clay MMT have been prepared by simple solution polymerization technique. The obtained CPs have been characterized using various techniques such as Fourier-Infra-red (FT-IR), scanning electron microscope (SEM), differential scanning calorimetric (DSC) and thermo gravimetric analysis (TGA). The prepared CPs has been used as potential adsorbents for removal of different toxic metal ions from their aqueous solutions. The CP containing MMT clay showed higher sorption capacity. The adsorption performance of the prepared CPs has been found to match well with Langmuir adsorption isotherms. The maximum sorption capacity for Cu⁺² ions was found to be 200.7 mg/g at natural pH 5.8 and was highly enhanced to reach 478.6 mg/g at higher pH values. The correlation coefficient values showed that the sorption of Cu⁺² ions by CP with and without clay fit well pseudo-second order models. The highest sorption affinity of the prepared CPs towards different metal ions was in the order Co > Ni > Pb > Cu > Cd > Cr and Pb > Cu > Cd > Ni > Co > Cr for CP without and with clay respectively.

Keywords: Chelating polymers, Copper ion uptake, Sorption kinetics, and Sorption affinity.

Nowadays heavy metal pollution has come to be one of the most serious threats for environment. Exposure to a trace of heavy metals is considered a risk for human beings⁽¹⁻⁴⁾. Thus, how to efficiently and extremely get rid of toxic heavy metals from water systems is still a very important but still interesting task for environmental engineers. Many technologies such as chemical precipitation, ion exchange, adsorption, membrane filtration have been adopted to remove poisonous metal ions from water⁽⁵⁻⁹⁾. Recently, numerous approaches have been discovered to develop low-priced and more effective technologies for water purification. Adsorption has proven to be cost-effective and competent for removing heavy metals, organic pollutants and dyes from water systems⁽¹⁰⁾. Adsorbents attracted vast attention due to accessibility of various adsorbent

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types, environmental friendly, cost viability, and their high effectiveness in removal of organic and inorganic pollutants. There are several important standards governing the selection and design adsorbents such as fast removal, ion selectivity and reusability^(11, 12).

Recently, adsorbents built on nanomaterials gained great attention due to their extraordinary performance to adsorb pollutants from aqueous environments such as carbon nanotubes, titania, silica and clay polymer composites⁽¹³⁻¹⁷⁾. Ionic polymer clay nanocomposites⁽¹⁸⁾ showed effectiveness for removal of inorganic and organic pollutants^(19, 20). The sorption capacity of polymer-clay composites was affected by preparation process, type of polymer-clay composites and application technique such as membrane, nano-filters, etc⁽²¹⁻²³⁾.

The use of (inorganic-organic) nanomaterials such as polymer clay composites as an adsorbent is regarded as one of the most effective methods for removal of heavy metal ions from aqueous phase⁽²⁴⁾. On other hand, structural flexibility, mechanical performance and prospective applications in harsh environmental conditions are some of the major merits of these hybrid polymeric materials. Research is working on synthesizing and testing the possibilities to apply these hybrid polymeric adsorbents for removal of toxic metal ions from aqueous solutions⁽²⁵⁻²⁹⁾.

Considering the merits of the aforementioned polymer- clay composites as adsorbents, in present study, we have synthesized new efficient, low-cost chelating polymers CPs based on cheap waste polymeric materials for efficient removal of some toxic heavy metal ions from their aqueous solutions.

Experimental

Materials

Copper acetate $(\text{CH}_3\text{COO})_2\text{Cu}\cdot 4\text{H}_2\text{O}$, cobalt acetate $\text{Co}(\text{Ac})_2\cdot 4\text{H}_2\text{O}$, nickel acetate $\text{Ni}(\text{Ac})_2\cdot 4\text{H}_2\text{O}$, $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$, cadmium acetate $\text{Cd}(\text{Ac})_2\cdot 2\text{H}_2\text{O}$, lead acetate $\text{Pb}(\text{Ac})_2\cdot \text{OH}$, $\text{Cu}(\text{Ac})_2\cdot \text{H}_2\text{O}$, butyl acrylate BA and itaconic acid IA are products of Sigma Aldrich, Saint Louis, Missouri, USA. All other chemicals used were chemically pure and are products of Prolabo Chemical Company (BDH, England).

Characterization techniques

Infra-red spectra IR

IR analyses of the prepared CPs have been measured using Jasco 6100 plus FT-IR spectrometer, Japan.

Differential scanning calorimetric analysis (DSC) and thermo-gravimetric analysis (TGA)

Thermal analyses TGA and DSC for the tested samples have been measured using a Perkin Elmer, thermogravimetric analyzer, USA, under nitrogen conditions. The heating rate was 10°C per minute from 50°C to 500°C.

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Scanning electron microscope/energy dispersion X-ray (SEM/EDX)

Morphological studies as well as element constitution of the tested samples have been measured using SEM /EDX (JEOL JXA- 840 A Electron PROBE), microanalyzer microscope, Japan.

UV-VIS spectrophotometer

Spectrophotometric measurements were carried out using UV-vis (JASCO V-630) spectrophotometer, Japan.

*Synthesis of chelating polymers CPs**In presence of MMT clay*

The synthesis reaction was done according to previous work by Elhalawany *et al.* ⁽²¹⁾ and it is in detail as follows: First, 6g WPMMA and 0.2 g MMT were soaked in 25 ml dioxane and then homogenized using Greaves homogenizer X120, Germany at 6000 rpm for 10 min. The previous homogenized solution was charged into 100 ml two-neck flask fitted with a reflux condenser followed by the addition of 0.2 g benzoyl peroxide PBO dissolved in 5 ml dioxane and (9.6×10^{-3}) moles BA dropwisely under continuous stirring at 750 rpm at 75°C. The reaction was left for 2 hr to form the seed polymer. Finally a (3.8×10^{-3}) mole of IA was added to the reaction media. The polymerization reaction was left for further 2 hr. The resultants CP have been purified by washing with water / methanol mixture of ratio (3:1) several times to remove the unreacted water soluble monomers followed by soxhlet extraction from diethyl ether to remove the excess initiator and the unreacted BA monomer.

In absence of clay

The reaction was done as the aforementioned procedure.

Determination of equilibrium swelling values (ESVs) of CPs

A known amount of dry polymer was immersed in distilled water at room temperature and held there at different times, and then weighed. The ESV of the CPs was determined gravimetrically by using the following equation:

$$\text{ESV (gH}_2\text{O/g}_{\text{CP}}) = (w_s - w_d) / w_d \quad \text{Eq (1)}$$

where w_s and w_d are the weights of swollen and dry CPs, respectively.

*Metal ion uptake measurements**Preparation of Cu (II) solution*

Stock solution of copper ion of initial concentration C_i (7.852×10^3 mg/L) has been prepared by dissolving 1.963×10^3 mg copper acetate in 250 ml distilled water.

Copper ion uptake experiments

A 0.3 g of the obtained CPs was placed into separating funnel with sintered glass filter system containing 30 ml of copper acetate solution of well-known initial concentration (C_i) at room temperature for a definite time. The residual concentration (C_r) of the copper ion under investigation was determined using UV-Visible (UV-vis)

spectrophotometer via different absorption/concentration standard curves. The copper ion uptake (CIU) was determined according to Equation 2:

$$q_e = V (C_i - C_r) / m \quad \text{Eq (2)}$$

where C_i and C_r are the initial and final metal ion concentration (mg/L), respectively, V is the volume of solution (L) and m is the mass of the dried CPs (g).

Effect of pH on the uptake of copper ion

Uptake experiments under controlled pH were carried out following the above procedure for uptake experiments. The pH was adjusted using the suitable buffer.

Competitive removal of metal ions from aqueous solution

A mixture solution containing (Cr^{+3} , Co^{+2} , Ni^{+2} , Cu^{+2} , Cd^{+2} , Pb^{+2}) ions of concentrations (1281, 1057, 1051, 197.5, 592.7, 331.4) mg/L respectively was added to 0.05g of dry CP at room temperature and left for two hours. The percentage of adsorbate ions onto the CP was determined by EDAX (JEOL JXA-840 A Electron PROBE) microanalyzer microscope.

Results and Discussion

The resultant CP in presence of MMT is supposed to have the following conceptual structure and it is represented in Fig.1.

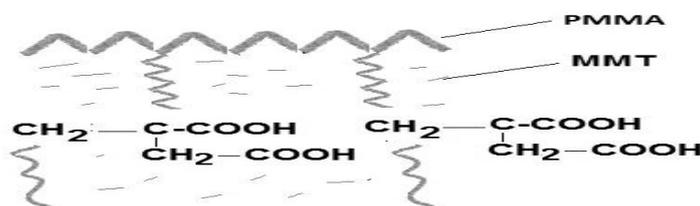


Fig.1. Conceptual structure of the prepared CP in presence of MMT clay.

The proposed mechanism for the interaction of the prepared CPs with the studied copper ions is illustrated in Fig. 2.

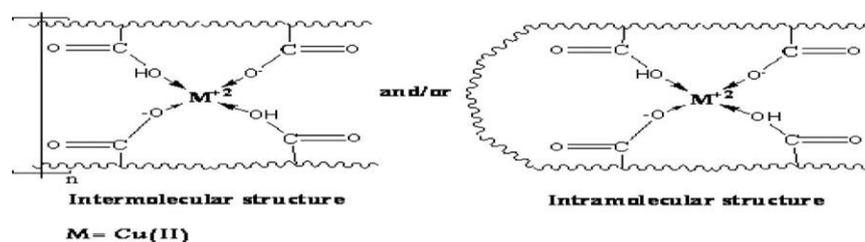


Fig. 2. The interaction of the prepared CPs with the tested copper ion.

*Characterization of the prepared CPs**FT-IR spectra*

The FT-IR spectra of CPs with and without clay are represented in Fig. 3. The adsorption bands at 3438, 1452 cm^{-1} are attributed to the stretching and bending of O-H group of IA. The adsorption bands at 1732 and 1156 cm^{-1} are attributed to C=O and C-O stretching of ester group of BA and PMMA. The adsorption band at 1159 is attributed to -O-CH₃ stretching vibrations⁽³⁰⁾.

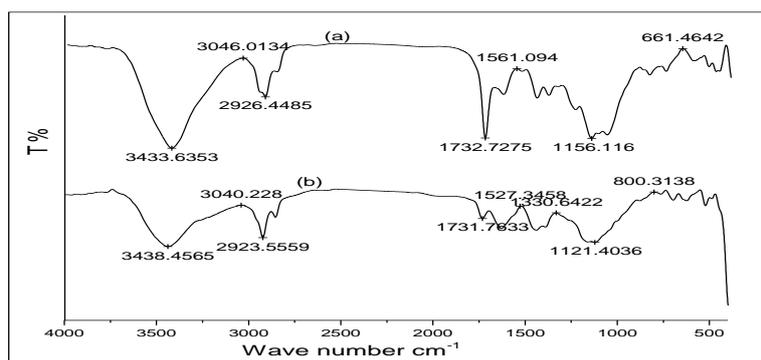


Fig. 3. FT-IR spectra of the prepared CPs a) without clay and B) with clay.

Thermo-gravimetric analysis (TGA)

Thermo gravimetric analyses for the prepared CPs are shown in Fig. 4. It is clearly seen from the figure that there are two major stages of weight loss for grafted PMMA with IA; where in the first stage the weight losses of CP with and without clay are 30.88% and 26.5% at temperatures 363.01°C and 337.35°C, respectively. On the other hand the weight losses of CP with and without clay in the second stage is 57.96% and 66.48% at temperatures 399.42°C and 372.69°C. The CP containing clay showed higher thermal stability. In general, it can be concluded that the presence of slight amount of MMT clay enhances the thermal stability.

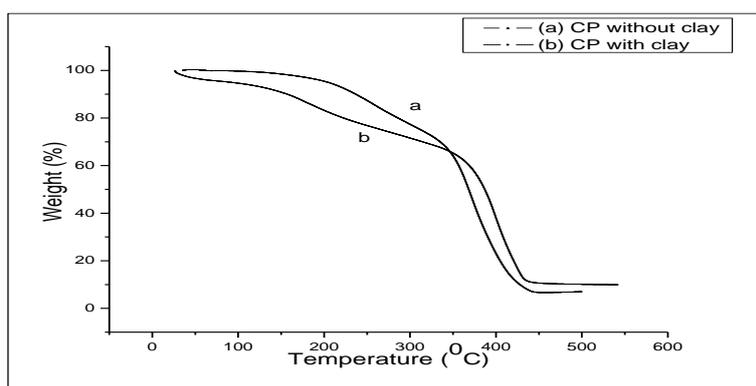


Fig. 4. TGA of the prepared CPs (a) without clay and (b) with clay.

Differential scanning calorimetry (DSC)

Figure 5 shows DSC thermograms of the prepared CPs in absence and presence of MMT clay. The glass transitions temperature (T_g) appear at 75.50 and 168.91°C for CP without and with clay, respectively. In addition, the endothermic melting transitions for CP without and with clay appear at 75.50 and 168.91°C, respectively.

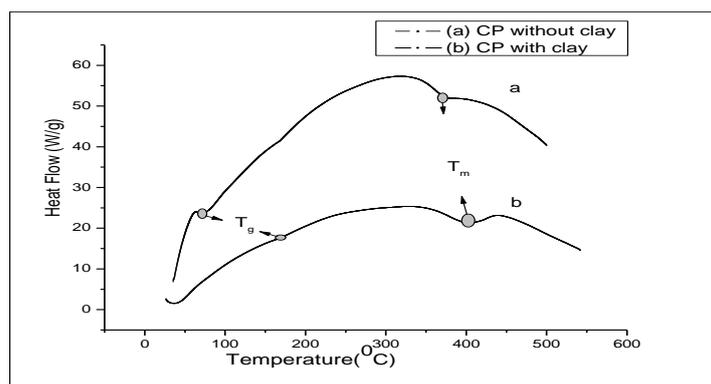


Fig. 5. DSC curves for the prepared CPs (a) without clay and (b) with clay.

Scanning electron microscope (SEM)

Scanning electron microscope (SEM) analysis for the prepared CPs in presence and absence of MMT clay is shown in Fig. 6. Figure 6 showed that the CP without MMT showed that the CP with MMT is more porous than that without clay which increases the efficiency of metal ion removal indicating well dispersed MMT nanoparticles through the polymer matrix and this morphological situation is believed to be responsible for enhanced sorption capacity.

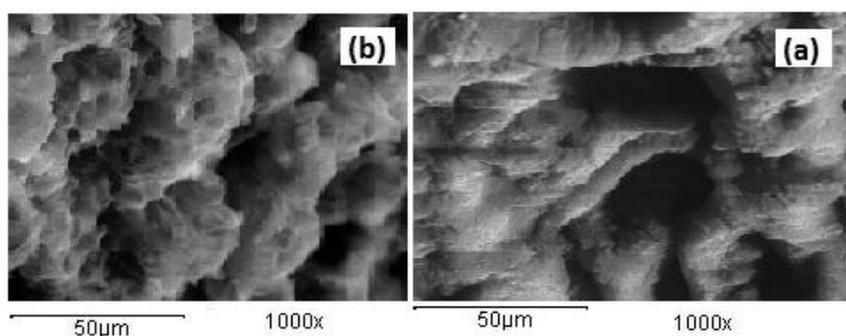


Fig. 6. SEM for the surface morphology of CPs (a) without clay and (b) with clay.

Equilibrium swelling values (ESVs) of CPs

Equilibrium swelling values (ESVs) by the prepared CPs at different time intervals is shown in Fig. 7. It is clearly seen from the figure that the equilibrium swelling values (ESVs) of CPs by the prepared CPs are fixed in the rise and fall sequentially.

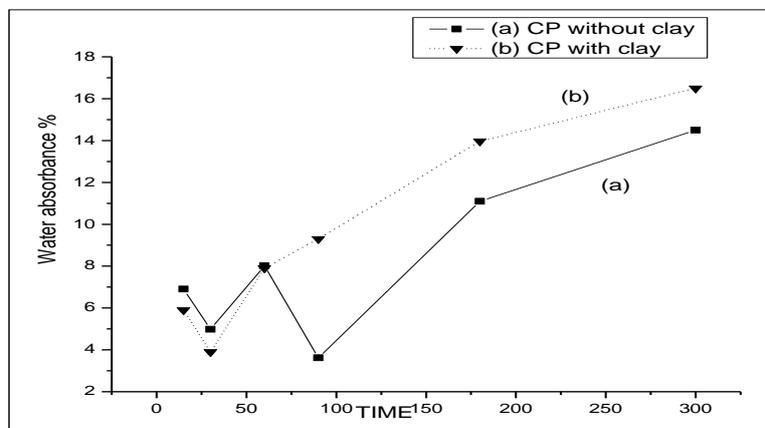


Fig. 7. Equilibrium swelling values (ESVs) by the prepared CPs (a) without clay and (b) with clay at different time intervals.

Sorption kinetics

Effect of contact time

The copper ion uptake CIU by the prepared CPs (0.3g) at natural (pH 5.8) and at different time intervals is shown in Fig. 8. It is clearly seen from the figure that fast CIU is fixed in the rise and fall sequentially, we find that the highest percentage of them were withdrawn at 40 min for CP without and with clay, respectively. This is identical with the results of the water absorption for both CPs. It is clearly seen from the data that the maximum sorption capacities for Cu^{+2} ions were 200.7mg/g and 200mg/g mg/g for CP with and without clay, respectively.

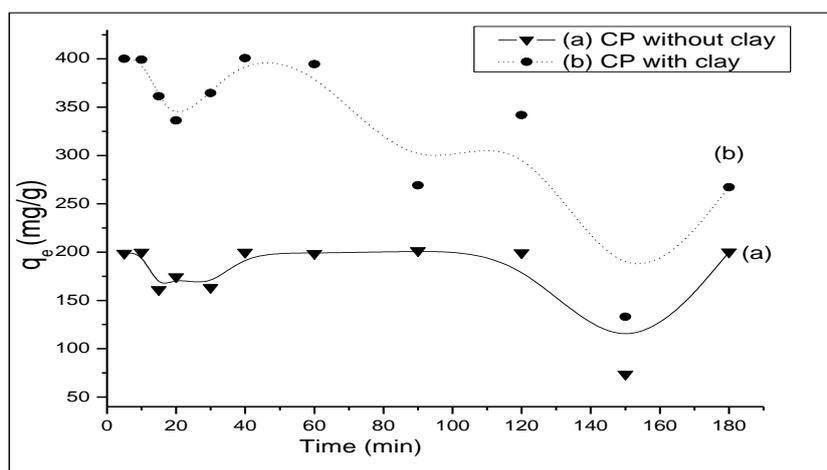


Fig. 8. Sorption of Cu^{+2} ions by the prepared CPs (a) without clay and (b) with clay at different time intervals.

Kinetics of Cu(II) sorption

The kinetics of Cu⁺² ion sorption can be demonstrated using two basic kinetic models including pseudo-first and pseudosecond order. The pseudo-first-order model is expressed by Lagergren (1898)⁽³¹⁾ as:

$$\text{Log } (q_e - q_t) = \log q_e - K_1 t / 2.3 \quad (3)$$

where k_1 is the pseudo-first-order rate constant (min^{-1}) of adsorption and q_e and q_t (mmol/g) are the amounts of metal ion adsorbed at equilibrium and time t (min), respectively. On the other hand, the pseudo-second order model is expressed by Ho and Mckay⁽³²⁾ as:

$$t/q_t = 1/K_2 q_e + t/q \quad (4)$$

where k_2 is the pseudo-second-order rate constant of adsorption. The above-mentioned two models basically considering external film diffusion, intraparticle diffusion and interaction step for adsorption process. The rate determining step of adsorption reaction may be one of the above three steps (Donia *et al.*, 2008)⁽³³⁾.

The kinetic parameters for the pseudo-first and pseudo-second models were determined from the linear plots of $\log (q_e - q_t)$ versus t and (t/q_t) versus t , respectively as shown in Fig. 9 & 10 and Table 1. The validity of each model could be checked by the fitness of the straight lines according to the values of correlation coefficients (R^2 values).

It is clearly seen from the figures and correlation coefficient values that the sorption of Cu⁺² ions by the prepared CP in presence and absence of clay fit well pseudo-second-order model. And this indicated that the sorption of Cu⁺² ions depends on both the concentration of Cu⁺² ions and adsorbent.

TABLE 1. The kinetic parameters for pseudo-first-order and pseudo-second-order models .

Sample	First Order		Second Order	
	K_1	R^2	K_2	R^2
CP without clay	0.0262	0.8007	9.65×10^{-3}	0.8133
CP with clay	7.4038×10^{-4}	0.02769	9.329×10^{-3}	0.94358

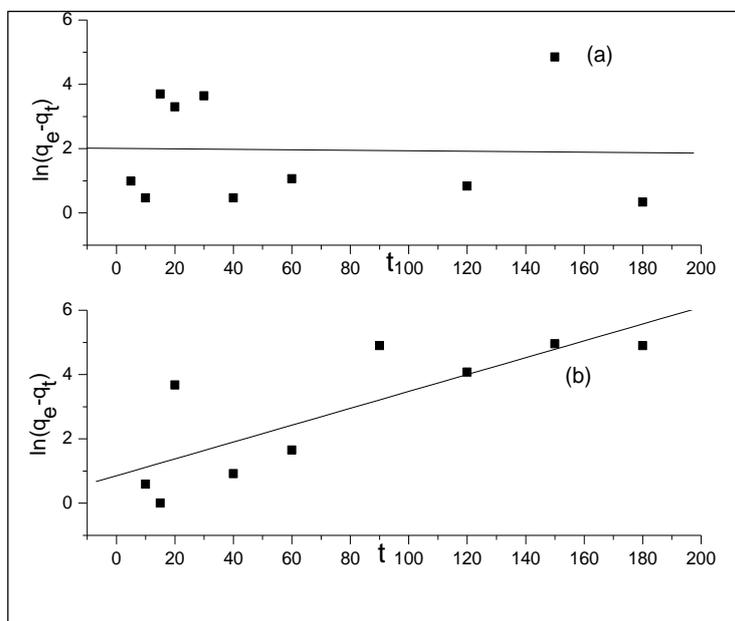


Fig. 9. The First order plots for (a) CP without clay and (b) with clay.

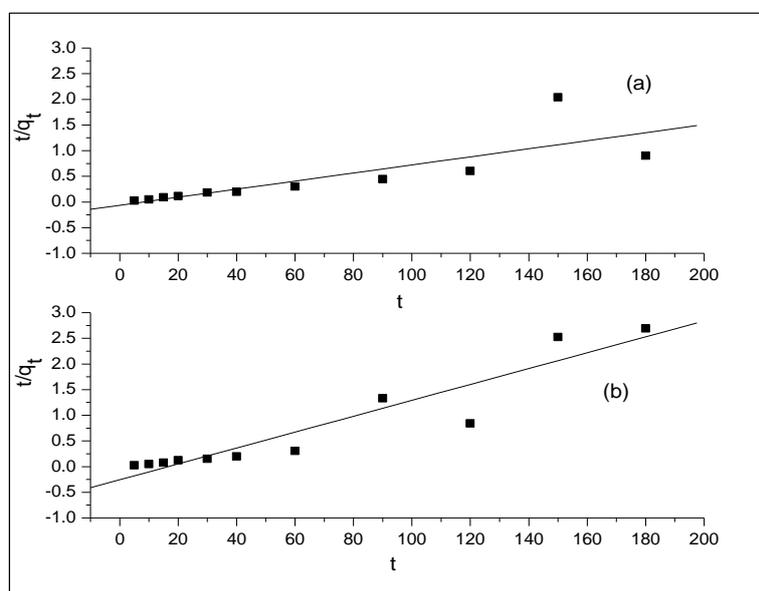


Fig.10. The Second order plots for (a) CP without clay and (b) with clay.

Adsorption isotherms

Equilibrium data, commonly known as adsorption isotherms, are crucial necessities for the design of adsorption systems. These data give information on the capacity of the adsorbent or the amount necessary to eliminate a unit mass of pollutant under the system conditions ^(34, 35).

In order to adjust the design of a sorption system to remove pollutants from effluents, it is important to set up the most proper correlation for the equilibrium curve. Two isotherm equations have been tested in the current study, namely, Langmuir and Freundlich. This modelling allows us to define the maximum capacity of removal. The quality of the isotherm to fit the experimental data is normally verified according to the value of the correlation coefficient (R^2), *i.e.* the isotherm giving R^2 value closest to unity is considered to provide the best fit.

Langmuir isotherm : The Langmuir adsorption model assumes that the molecules are adsorbed at fixed number of definite sites, each of which can only hold one molecule and no transfer of adsorbate in plane of the surface. These sites are also supposed to be energetically equivalent and far away from each other, so that there are no interactions between the molecules adsorbed to neighboring sites. The linear form of the Langmuir isotherm is represented by the following equation ⁽³⁶⁾.

$$C_e / q_e = C_e / Q_{\max} + 1 / Q_{\max} K \quad (5)$$

where q_e is the amount of metal ion sorbed per unit weight of adsorbent (mg/g), C_e the equilibrium concentration of the metal ion in the equilibrium solution (mg/l), Q_{\max} (mg/g) is the monolayer adsorption capacity and K (L/mg) is Langmuir constant that related to the adsorption heat energy. The results obtained from the Langmuir model for CIU by the prepared CPs are shown in Table 2 and Fig. 11. The values of maximum monolayer capacity Q_{\max} obtained from Langmuir isotherm indicate that the CP with clay has higher sorption capacity than that of clay free.

Freundlich isotherm: Freundlich isotherm is an empirical equation that involves the heterogeneity, the exponential distribution of sites, and their energies. The sorption data have been analyzed using the logarithmic form of the Freundlich isotherm as shown below ⁽³⁷⁾ :

$$\text{Log } q_e = N \text{ log } C_e + \text{log } K_f \quad (6)$$

where K_f (mg/L) and N are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The value of term N in the Freundlich isotherm model shows the nature of isotherm to be unfavorable ($N > 1$), favorable ($0 < N < 1$) or irreversible ($N = 0$). The results obtained from the

Freundlich model for CIU by the prepared CPs are shown in Table 2 and Fig. 12. The correlation coefficients values deduced from Freundlich equation showed that the Freundlich model is comparable to the Langmuir model. The N values reported in Table 2 are lower than 1 indicating that Cu^{2+} ions sorption by the prepared CPs is favorable.

The correlation coefficients values listed in Table 2 indicated that the Cu^{2+} ions sorption process matches more with Langmuir adsorption model than that of Freundlich.

TABLE 2. Different adsorption models parameters and coefficients for Cu^{2+} ions sorption.

Sample	Langmuir			Freundlich		
	Q_{\max}	K	R^2	K_f	N	R^2
CP without clay	74.851	0.011848	0.97348	45.4046×10	0.2014	0.83595
CP with clay	62.814	0.011879	0.98073	58.9223×10	0.27832	0.88889

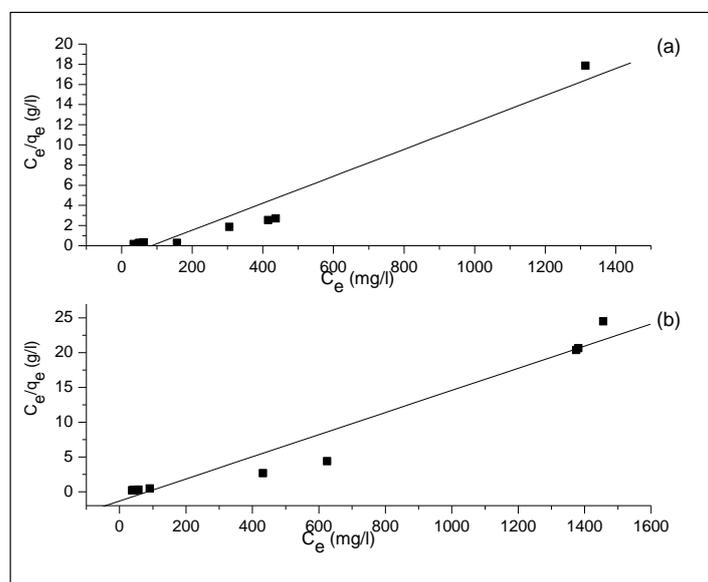


Fig. 11. The Langmuir isotherm plots for (a) CP without clay and (b) CP with clay.

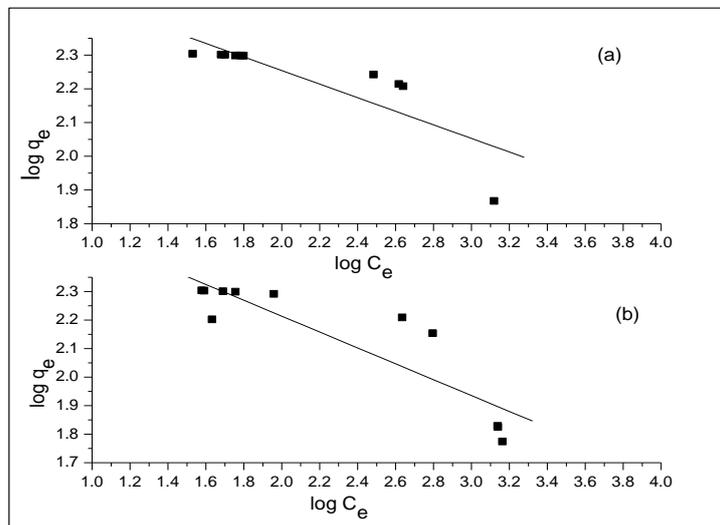


Fig. 12. The Freundlich isotherm plots for (a) CP without clay and (b) CP with clay.

Effect of pH

Figure 13 shows the uptake of Cu^{+2} ions by the obtained chelating polymers (CPs) at different pH values. It is shown from the figure that the MIU increases as the pH increases. At lower pH value (1 & 3) the dissociation of the carboxylic acid groups is limited and hence reduces the chelation with different metal ions, but at higher pH value (8.5 & 10), ionization of carboxylic acid groups takes place which cause these polymers to undergo a transition from a compact form to an extended form upon the ionization of the primary carboxyl group⁽³⁸⁾ and hence an increase in the metal ion uptake occurs.

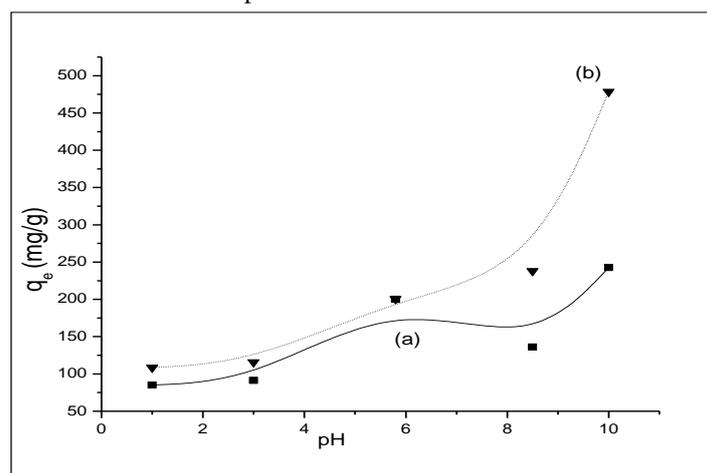


Fig.13. Uptake of Cu^{+2} by CP without clay and CP with clay as a function of pH.

Selectivity measurements

Since various metal ion pollutants may present in drinking water as well as wastewater, it is essential to investigate the competitive binding affinity of these ions towards the prepared CPs. The elements constitutions of the tested CPs were detected by the EDAX using a standard less qualitative (EDAX) analytical technique. The peak heights in the EDAX spectra are proportional to the metallic elements concentration which is chemisorbed⁽³⁹⁾. The EDAX spectrum for (Cr^{+3} , Co^{+2} , Ni^{+2} , Cu^{+2} , Cd^{+2} , Pb^{+2}) ions is illustrated in Fig. 14. It could be seen that all previously mentioned metal ions became one element of solid sample in this spectrum and that can be explained as those ions may be chemisorbed on the surface of the CPs as shown in Fig. 15. Elemental constitution is illustrated in Table 3. The sorption capacities of the tested metal ions are in the order $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+}$; for CP with clay and in the order $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Cr}^{3+}$ for CP free of clay as shown in Fig. 16 and Table 3.

TABLE 3. Elemental constitutions (%) by EDAX analyses.

CPs	Metal ions Weight %					
	Cr	Co	Ni	Cu	Cd	Pb
Without clay	7.14	27.03	22.48	16.42	8.63	18.29
With clay	0.89	1.12	4.25	8.67	6.02	84.29

**Fig. 14. EDAX spectrum of grafted waste under: (a) adsorbed without clay; (b) with clay.**

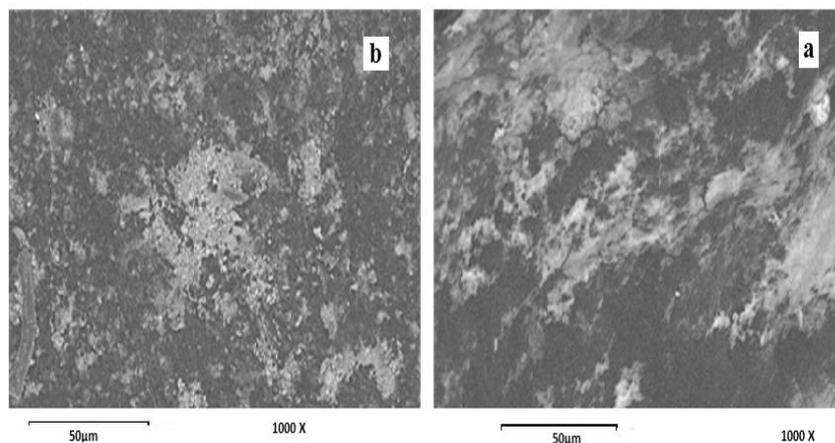


Fig. 15. EDAX for the surface morphology of CPs (a) without clay and (b) with clay.

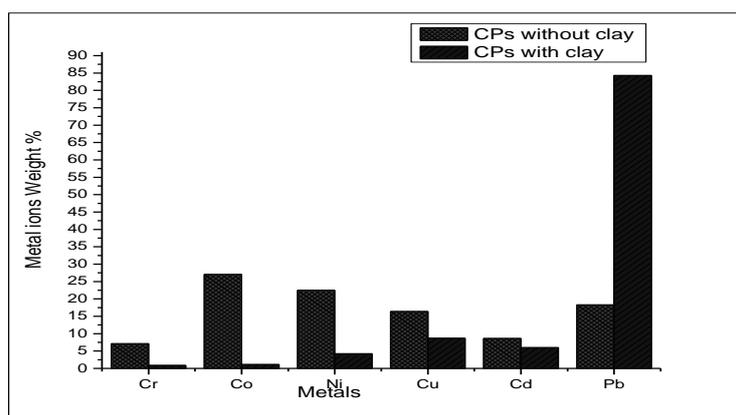


Fig. 16. The competitive binding affinity of the tested metal ions towards the prepared CPs.

Finally, we can conclude that the prepared chelating polymers CPs in this study have given promising results compared to those reported by the traditional chelating resins. The maximum sorption capacity reported in our study for Cu^{+2} ions is much higher than that reported by Ramazan Coskun *et al.* ⁽⁴⁰⁾, Deniz Türkmen *et al.* ⁽⁴¹⁾, Jinnan Wang *et al.* ⁽⁴²⁾, Fei Ji *et al.* ⁽⁴³⁾ and Hyonggoo Yoo and Seung-Yeop Kwak ⁽⁴⁴⁾ as shown from Table 4. In addition, the maximum sorption capacity for the studied metal ion is highly increased at elevated pH values.

TABLE 4. Sorption capacity of different chelating resins.

Chelating polymers	Sorption capacity	References
CP without clay	200mg/g	Present study
CP with clay	200.7mg/g	Present study
methacrylic acid/acrylamide monomer mixture grafted poly(ethylene terephthalate) fiber	31.25 mg/g	Ramazan Cos_kun <i>et al.</i> 2006
Poly(hydroxyethyl methacrylate)	58 mg/g	Deniz Türkmen <i>et al.</i> 2009
hyper-crosslinked polystyrene	75mg/g	Jinnan Wang <i>et al.</i> 2011
Cellulose acetate (CA)/zeolite (Z) composite fiber	28.57 mg/g	Fei Ji <i>et al.</i> 2012
hyperbranchedpoly(amidoamine)-graftedpoly(tetrafluoroethylene)	14.2mg/L	Hyonggoo Yoo and Seung-Yeop Kwak 2013

Conclusion

In this study a new easily prepared, low-cost and efficient chelating polymers CPs based on waste polymethylmethacrylate plastics have been used as potential adsorbents for removal of toxic heavy metal pollutants from water system. The adsorptions of Cu^{2+} ions were found to be time dependent. Adsorption isotherms have been studied in terms of Langmuir and Freundlich isotherms models. The values of correlation coefficients deduced from the aforementioned two models confirmed that Cu^{2+} ions sorption followed Langmuir adsorption model. The selectivity measurements for different toxic heavy metal ions have been investigated and it was found that the competitive binding affinity of the tested metal ions are in the order $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+}$; for CP with clay and in the order $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Cr}^{3+}$ for CP free of clay. The metal ion uptake increases with increasing pH values due to complete ionization of the COOH groups occurred at higher pH values.

Finally, we can conclude that this commercial, easily prepared CPs have double positive features in which it helps to get rid of the organic plastic wastes as well as toxic heavy metal pollutants.

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تحضير بوليمرات مخلبية ذات كفاءة عالية في ازالة العناصر الثقيلة من المخلفات البلاستيكية

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اعتمدت هذه الدراسة على تحضير بوليمرات مخلبية ذات كفاءة عالية في ازالة العناصر الثقيلة الملوثة للمياه من المخلفات البولى ميثيل ميثاكريلات المعدل بحمض الايتاكونيك تارة في وجود طفلة المونتمورلينييت واخرى في عدم وجودها . تم توصيف البوليمرات المخلبية المحضرة عن طريقة تقنية الاشعة تحت الحمراء، الماسح الالكترونى ، مقياس الكالورى والتحليل الحرارى. البوليمرات الخلية المحضرة في وجود الطفلة أبدت كفاءة عالية في سعة الامتزاز وتتبع لانجمير ايزو ثيرم.وقد أظهرت الاختبارات أن كمية امتزاز ايونات النحاس كانت 200.7مجم/جم وتزيد بزيادة درجة الحامضية لتصل الى 478.6مجم/جم. وبمقارنة نسبة امتزاز ايونات النحاس في وجود ايونات اخرى من العناصر الثقيلة كان ترتيب العناصر في غياب وجود الطفلة على التوالى .

Co>Ni>Pb> Cu> Cd> Cr and Pb> Cu> Cd> Ni> Co>Cr