

Removal Of Mercuric Ions (II) From Aqueous Solutions by Chelating Resin Containing Carboxylic Groups

J. Y. Hamdo⁽¹⁾

Received 13/06/2013

Accepted 20/08/2013

ABSTRACT

Pollution by heavy metals, due to their toxic nature and other adverse effects, is one of the most serious environmental problems. Many heavy metal ions, such as mercuric ions are detected in industrial wastewaters originating from metal plating, mining activities, paint manufacture, etc. This ion isn't biodegradable and tends to accumulate in living organisms, causing various diseases and disorders. Therefore, it should be removed from aqueous solution before discharge. In this paper it has been done an experimental work regarding the optimal conditions of removing mercury from water using ion exchange resins namely maleic acid–vinyl acetate copolymer (PMA-VA). The adsorption behavior of mercury ions on PMA-VA was studied as a function of the following variables: contact time, pH solutions, initial concentration of metal ions, resin dosage, and ionic strength. Equilibrium studies showed that, the maximum adsorption capacity of adsorbent for mercuric ions was: 0.75 mmol/g PMA-VA. Regeneration of PMA-VA resin is possible by treatment with appropriate diluted mixtures of nitric acid and sodium nitrate. The results show that, PMA-VA resin holds great potential to remove mercuric ions from polluted wastewater.

Keywords: Adsorption, Chelating resin, maleic acid–vinyl acetate copolymer, Carboxylic Groups, Mercuric Ion(II).

⁽¹⁾ Prof., Department of Chemistry, Faculty of Sciences, Damascus University, Syria.

إزالة أيون الزئبق (II) من محاليله المائية باستخدام ريزين مخلب ذي مجموعات وظيفية كربوكسيلية

جمال يونس حمدو⁽¹⁾

تاريخ الإيداع 2013/06/13

قبل للنشر في 2013/08/20

الملخص

يعدُّ التلوث بالعناصر الثقيلة أحد أهم المشكلات البيئية وأخطرها، نظراً إلى طبيعته السمية وأثاره السلبية المتعددة في البيئة. كُشف عن العديد من أيونات العناصر الثقيلة، ولاسيما أيون الزئبق (II)، في مياه المخلفات الصناعية الناتجة عن الطلاء المعدني وصناعة الأصبغة وعمليات التعدين. تكمن المشكلة الأساسية لوجود هذا الأيون في المياه العادمة في أنه لايتحلل ويمكن أن يتراكم في الكائنات الحية، مما يتسبب في أمراض واضطرابات مختلفة للإنسان. لذلك كان لا بد من إيجاد طريقة مناسبة للتخلص من هذا الأيون قبل رمي مياهه إلى البيئة. يعرض هذا البحث النتائج التجريبية لاستنباط الظروف المثلى لإزالة أيون الزئبق (II) من المياه العادمة باستخدام ريزين التبادل الأيوني حمض المالنك- أستات الفينيل PMA-VA. درست مختلف العوامل التي تؤثر في السعة الامتزازية للريزين مثل زمن التوازن والتركيز الابتدائي للأيون المدروس وكمية الريزين وحموضة الوسط والقوة الأيونية. كانت السعة الامتزازية العظمى للريزين تجاه هذا الأيون نحو $0.75 \text{ mmol(Hg}^{2+})/\text{g}$ من الريزين PMA-VA. درست أيضاً إمكانية الاستخدام المتكرر للريزين بإعادة تنشيطه، بالمعالجة بمحلول مخفف من حمض النتريك ونترات الصوديوم. يستدل من نتائج الدراسة على تمتع الريزين بإمكانية كبيرة في نزع أيون الزئبق (II) من المياه الصناعية الملوثة.

الكلمات المفتاحية: الامتزاز، الريزينات المخلبة، البوليمر المشترك حمض المالنك- أستات الفينيل، المجموعات الوظيفية الكربوكسيلية، أيون الزئبق (II).

⁽¹⁾ أستاذ، قسم الكيمياء، كلية العلوم، جامعة دمشق، سورية.

1- Introduction

Pollution by heavy metals, due to their toxic nature and other adverse effects, is one of the most serious environmental problems [1]. Many heavy metal ions, such as lead, cadmium, copper, and mercury, are detected in industrial wastewaters originating from metal plating, mining activities, paint manufacture, etc. These heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders [2]. Therefore, they must be removed from aqueous solution before discharge.

Mercury is well known for its extremely high toxicity and the serious threat to human life and natural environment. The drinking water criterion for mercury established by United States Environmental Protection Agency (USEPA) is 2 $\mu\text{g/L}$ and the permitted discharge limit of wastewater for total mercury is 10 $\mu\text{g/L}$. Therefore, it is very important to reduce the residual mercury concentration below the safety limit for mercury ions from industrial wastewater, especially from drinking water [3].

Several methods such as evaporation, electro-deposition, solvent extraction, reverse osmosis, membrane separation process and activated carbon adsorption are employed for the removal of heavy metal ions from water waste [4]. However, these techniques have certain disadvantages such as higher operational cost, requiring additional chemical, high energy consumption and residual metal sludge disposable. Due to forbidding cost of these processes, the uses of resins have been received with considerable attention [5]. In the recent years a number of commercial resins such as Amberlite IR-120, Amberlite IRC-748, Amberlite IRC-718, Lewatit TP-207 and a wide range of anion exchange resins with styrenic structures have been used to remove heavy metals from wastewater[6-9].

It is well known in the literature that, carboxylic functional groups can form metallic complexes and behave as ion exchangers. This property provides a wide range of applications to the copolymer maleic acid-vinyl acetate (PMA-VA), which contains in its structure carboxylic groups. This copolymer in its soluble form, can form stable complexes with most of heavy metal ions, which makes it useful as masking agent for trivalent charged cations in their spectrophotometric interferences with bivalence cations [10]. Also researchers used the soluble form of this copolymer for preparing selective membrane, which can be used in preparing ion selective electrode for Cu^{2+} [11]. In addition, the copolymer PMA-VA was used as ion exchanger for some heavy metal ions[12] and fluoride after

modified procedure in which PMA-VA turned into a positively charged complex with high charged cations, which reacts with fluoride in aqueous solutions [13].

In this paper, it has been done an experimental work regarding the optimal conditions of removing mercuric ions (II) from aqueous solutions using insoluble form of maleic acid–vinyl acetate copolymers (PMA-VA) .

2- Material and Methods

2.1 Ion-exchange resin:

The insoluble PMA-VA copolymers was prepared and purified in the laboratory as described by Al-kurdi et al [13], with one exception that, the percentage of cross-link agent was 2 %, which gives the synthesised copolymer more flexibility, subsequently less time is needed to reach equilibrium between copolymers and metal ions. The properties of the resin are given by Hamdo [12]. The resin was washed with double distilled water to remove impurities and dried in an oven at 60°C for 24 h. Dried resin was used for further experimental studies.

2.2 Determination of Carboxylic group content of PMA-VA :

The carboxylic group content of PMA-VA was determined by the back titration method [14]. 0.1 g sample was treated with 100 mL 0.01 mol/L KOH standard solution by stirring at room temperature for 1 hr. Several drops of phenolphthalein indicator were added. The above solution was back-titrated against 0.01 mol/L standard HCl solution until the solution turned from the pale pink to colorless. The carboxylic group content of PMA-VA was calculated by using the following equation:

$$C_{COOH} (mmol.g^{-1}) = \frac{V_{KOH} C_{KOH} - V_{HCl} C_{HCl}}{m}$$

where V_{KOH} and V_{HCl} are the volume of standard KOH used and standard HCl consumed, respectively, C_{KOH} and C_{HCl} are the molarity of standard NaOH and HCl, respectively, and m is the weight of the analyzed sample. The content of Carboxylic group is 3.84 ± 0.13 mmol/g PMA-VA.

2.3 Apparatus and Reagents:

A UV/Vis. Spectrophotometer model optizen 2120 uv plus, was used for the spectrophotometric determination of metal ions in solutions. The pH measurements were made with martin pH meter, model Mi 180.

All used chemicals were of analytical grade, and distilled water was used throughout the study. An Hg(II) stock solution 1000 mg L⁻¹ was prepared by dissolving 1.6195 g of mercury nitrate [Hg(NO₃)₂, Merck, Germany] in double distilled water acidified with 5mL of 5N HNO₃ to prevent hydrolysis and diluting to 1000mL. A working solution for the experiments was freshly prepared from the stock solution. The working solutions with different concentrations of Hg(II) were prepared by appropriate dilutions of the stock solution immediately prior to their use. The concentration of mercury (II) was determined by spectrophotometric method, using diphenylthiocarbazone as spectrophotometric reagent[15].

2.4 Adsorption Studies

All the adsorption studies were conducted by mixing 100.0 mg of PMA-VA and 25.0 mL of mercury(II) in a flask with a magnetic stirrer at about 120 rpm at room temperature . The ionic strength of the metal ion solutions was controlled by adding NaNO₃. The pH value of solutions were adjusted with NH₃-HOAC buffer or Standard acid 0.1 M HNO₃ and a base solution 0.1 M NaOH .After the equilibrium, the PMA-VA-metal ion complexes were separated from the solution by filtration. The concentrations of metal ions in the filtrates were determined spectrophotometrically.

The adsorption capacities Q (mg/g PMA-VA) were calculated by using the following equation:

$$Q = \frac{(C_0 - C_f)V}{m}$$

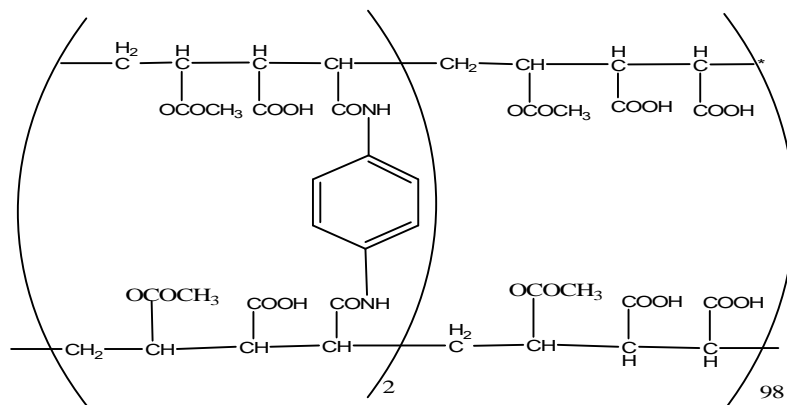
The percentage mercury removal, R(%) was calculated for each run by equation:

$$R\% = \frac{(C_0 - C_f)V}{C_0} \times 100\%$$

where C_0 and C_f are the initial and final concentrations (mg/L) of Hg(II) ion in the aqueous solution, respectively, V (L) is the volume of metal ion solution, and m is the added weight of PMA-VA (g). The same measurements were repeated three times and average values have been taken as the remaining metal amount in the solution phase.

3- Results and discussion

Maleic anhydride is well known to form the alternating copolymers with different monomers [16]. By the hydrolysis of this copolymer, carboxylic groups are formed (-COOH) regularly being in neighboring carbon atoms of every macromolecular unit. These groups have electron-donor properties which gives copolymer high ability to react with heavy metal ions. The formula of the base unit of maleic acid-vinyl acetate copolymers (PMA-VA) is shown in fig.1. The copolymer has a good thermal stability, and very good resistance to attrition and the action of solvents.



Maleic acid -vinyl acetate copolymer
(PMA-VA)

Fig.1. The formula of the base unite of PMA-VA after hydrolysis

3-1 Effect of the initial pH:

One important factor in metal ion removal from aqueous solutions is the pH, which can affect the adsorbent surface charge and the degree of ionization. The effect of initial pH on the removal of Hg(II) ions from aqueous solution was studied in the range of 1 to 7 pH. This range was chosen to avoid the precipitation of hydroxides. For these experiments 25 mL of Hg(II) solution was agitated with 100.00 mg of resin for a period of 60 minutes.

It can be shown from fig.2 that the removal Hg(II) increases with increasing pH of aqueous solution from (1.0-5.0) and then decreases.

The adsorption capacity of PMA-VA is low at low pH because large quantities of protons compete with mercury cations for the adsorption sites. As the pH of the solution increases, the number of protons dissociated from functional groups on the surface of PMA-VA increases and thus more negative groups for complexation of mercury cations are provided. Therefore, the electrostatic attraction increases between the mercury ions and the adsorbent, which leads to a higher adsorption capacity. The optimum pH values which correspond to the maximum adsorption capacity of Hg(II) were observed at pH5.

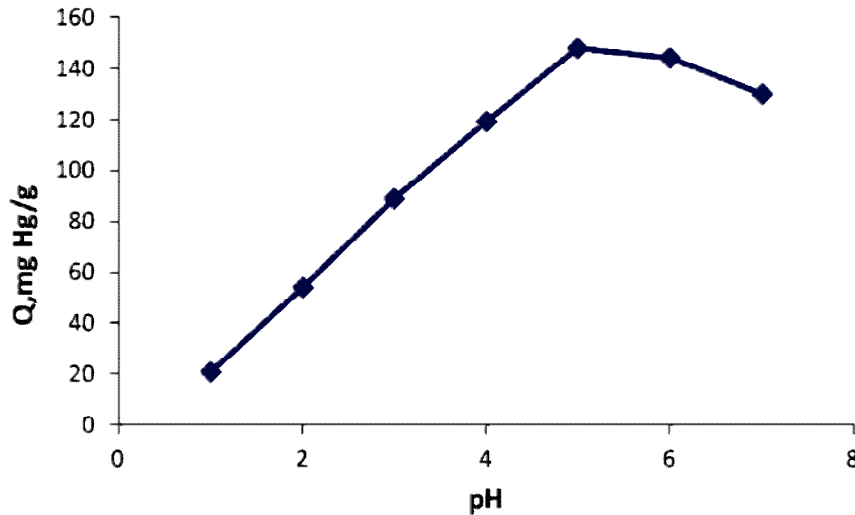


Fig.2 Effect of the pH on the adsorptions capacity of mercury ions by PMA-VA at $25.0 \pm 0.1^{\circ}\text{C}$ (initial concentration of metal ion = 4.99 mM; adsorption time = 60 min).

3-2 Effect of contact time:

Contact time is an important factor in evaluating the adsorption efficiency, which helps to determine the rate of maximum removal of solutes. The influence of contact time on adsorption capacity of Hg(II) are presented in Fig 3. The figure 3 shows that the removal percent of Hg(II) increases with contact time from 0-60 min and then becomes almost constant up to the end of the experiment. It can be concluded that the binding of Hg(II) with PMA-VA is high at initial stages and becomes almost constant after an optimum contact time of 60 min. The equilibrium adsorption capacity was about 0.75 mmol/g for

Hg(II). The optimum contact time correspond to the maximum adsorption capacity of Hg(II) was observed to be about 60 min.

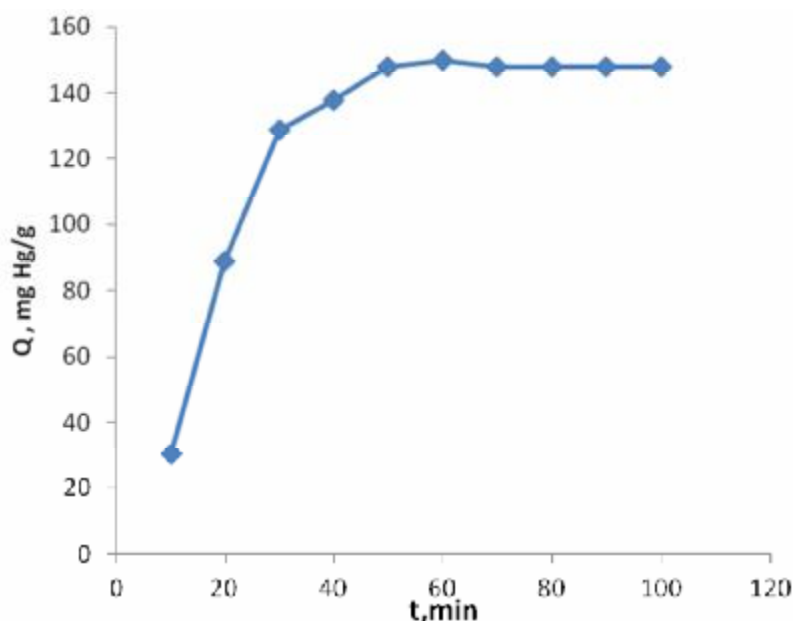


Fig. 3. Effect of adsorption time on the adsorption capacity of mercury ions at $25.0 \pm 0.1^{\circ}\text{C}$, pH5, initial concentration of mercury ions =4.99 mM).

It's assumed that, adsorption of mercury ions on proposed resin takes place according to two mechanisms: ionic exchange between hydrogen of carboxylic groups of resin and Hg(II) in solutions, and by internal diffusion through resin pores. The fact which supports the first mechanism is that, a considerable increase of acidity was noticed in solution after establishment of equilibrium. The other fact of ionic internal diffusion was affirmed by the rapid equilibrium between ions and resin, which was explained by large pores of resin produced by using low percentage of cross-linked agent, so ions can get in and out of resin readily. Also titration of released hydrogen ions in comparison with concentration of adsorbed ions by resin reveals that, the latter ions are in excess. The difference was attributed to presence of other adsorbed mechanisms than ionic exchange, such as internal diffusion and physical adsorption and so on.

3-3 Effect of resin amount

Adsorption of Hg(II) from a given solution (initial concentration of Hg(II) is 4.99 mM) was measured with different amount of PMA-VA resin in the range of 25.0 - 200.0 mg and equilibrated for 60 min. All experiments were carried out at the same conditions. Fig.4 shows variation of percentage removal of Hg(II) with resin dosage. It was found that the amount of adsorbed mercury ions increased with increasing amount of the resin up to 100.0 mg then adsorption capacity reaches almost a constant value. This result was expected because for a fixed initial metal concentration, increasing adsorbent amount provides greater surface area and adsorption sites [17].

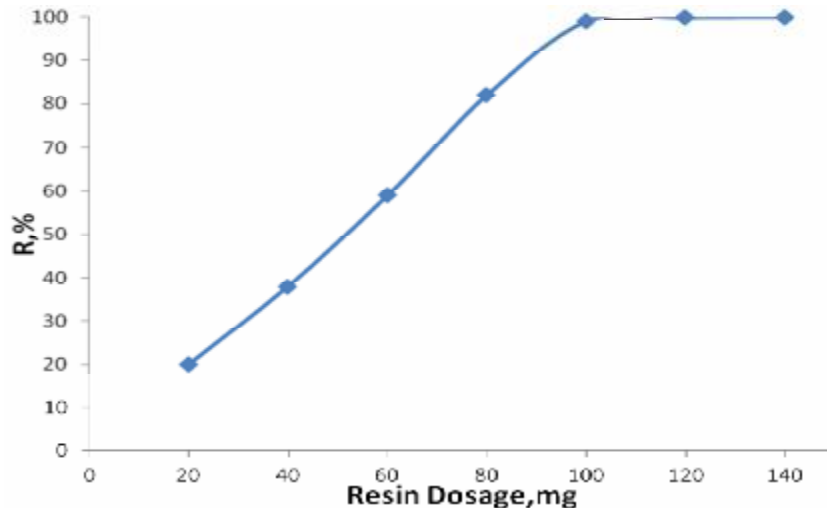


Fig.4 Effect of resin dosage on the ion exchange of mercury ions on PMA-VA resin, pH5, $t=25.0 \pm 0.1^{\circ}\text{C}$.

3-4 Effect of initial ion concentration on Adsorption

The influence of the initial concentration of Hg(II) on adsorption capacity is presented in Fig.5. The adsorption capacity increased first with increasing initial concentration of metal ion, then reached a plateau value. When the initial concentrations of mercury ions were less than 577.4 ppm, the quantity of adsorption sites in PMA-VA were vastly more than the amount of metal ion in tested solution. The high adsorption efficiency was attributed to the hydrophilic nature of carboxylate ($-\text{COO}^-$) groups in PMA-VA, which had an adequate affinity to the metal ions. Additionally, the long side chain of PMA-

VA acted as a spacer arm that could catch metal ions easily[18]. As the concentrations of metal ion increased, PMA-VA adsorbed more metal ions and the polymer chains shrunk. Hg(II) would be hard to diffuse toward the free chelating sites within PMA-VA. This is why the curves of adsorption capacity diverge at high concentrations of metal ions.

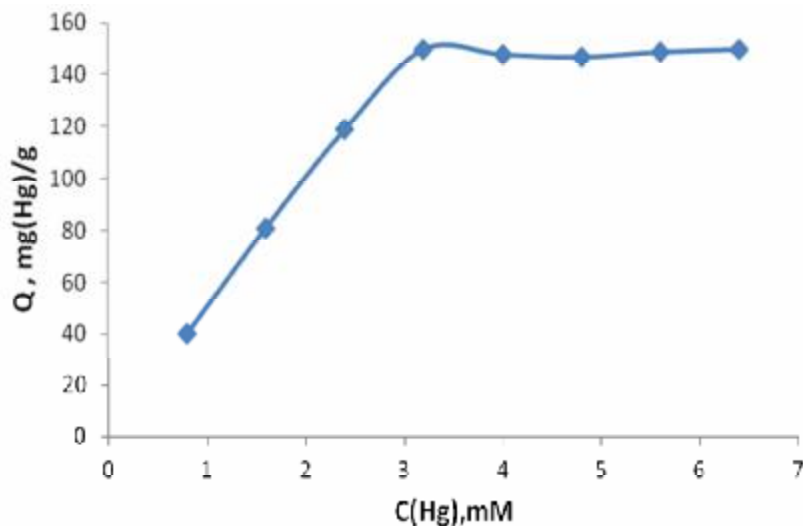


Fig.5 The influence of the initial concentration of mercury ions on the equilibrium adsorption capacity by PMA-VA at $25.0 \pm 0.1^{\circ}\text{C}$, pH 5 (adsorption time = 60 min).

3-5 Effect of ionic strength on Adsorption

The presence of salts in wastewaters is one of the important factors that may impede the adsorption of mercury ions. Fig.6 shows the adsorptions of Hg(II) by PMA-VA in the presence of 0 –1.0 mol/L of NaNO_3 . Obviously, as the concentration of NaNO_3 in aqueous solution increased from 0.1-0.5 M, the adsorption of Hg(II) decreased. As the concentration of NaNO_3 in aqueous solution increased more than 0.50 M, negative effect on the adsorption procedure is observed. The charge density of Hg(II) isn't so great to develop high attraction between the carboxylic group and Hg(II). Therefore, adsorption of Hg(II) is affected highly in the presence of NaNO_3 .

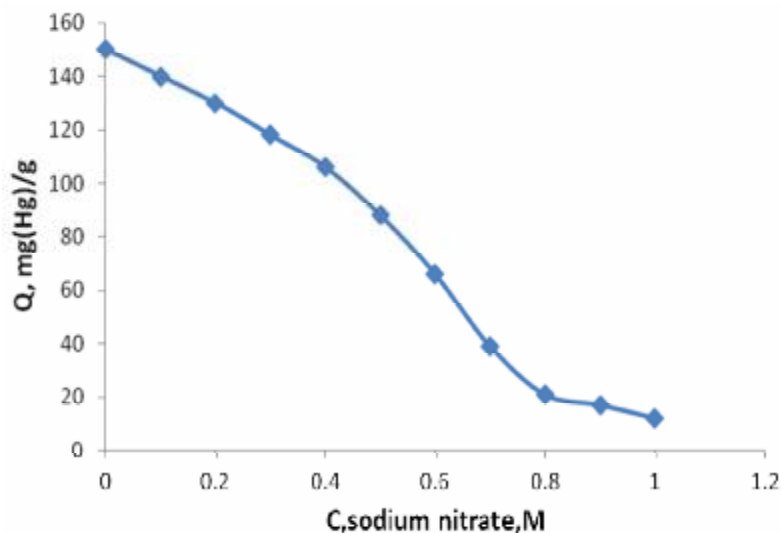


Fig.6 The adsorption of mercury ions by PMA-VA in the presence of NaNO_3 at $25.0 \pm 0.1^\circ\text{C}$, pH 5 (initial concentration of metal ion = 0.75 mM; adsorption time = 60 min).

3-6 Desorption and reuse

In practical application, it is very important to investigate the ability of an adsorbent to be regenerated and reused. Using a proper desorption solution, we can utilize the adsorbent repeatedly for the removal of heavy metal ions. Desorption of Hg(II) from PMA-VA – metal ion was carried out using 0.10 M HNO_3 + 0.20 M NaNO_3 solution at $25.0 \pm 0.1^\circ\text{C}$. The desorption process reached equilibrium at about 30 min and the desorption percent was approximately 98%. The results are taken as the mean of three values and RSD doesn't exceed 3.5% for all adsorption-desorption operations (tab.1). When PMA-VA–metal ions were placed in HNO_3 + NaNO_3 solution to release metal ions, H^+ and Na^+ could replace the metal ions adsorbed by carboxylic groups within PMA-VA to form carboxylic acids ($-\text{COOH}$) or salt ($-\text{COONa}$).

Table1. The adsorption capacities of PMA-VA after repeated adsorption–desorption operations at 25 °C, pH 5. Concentration of metal ion = 4.99 mM; Adsorption time = 60 min. Maximum adsorption capacity = 0.75 mmol (Hg²⁺)/g(PMA-VA) = 150.45 mg. (n=3,P=0.95,t=4.30)

Number of cycles	\bar{x} (mg/g PMA-VA)	s mg (Hg)	RSD,%	$\bar{x} \pm \frac{ts}{\sqrt{N}}$	R,% ~
Recycle 1	147.5	0.7	0.47	147.5±1.7	98%
Recycle 2	141.4	0.9	0.64	141.4±2.2	94%
Recycle 3	127.9	2.9	2.3	127.9±7.2	85%
Recycle 4	120.4	3.1	2.6	120.4±7.7	80%
Recycle 5	112.8	3.5	3.1	112.8±8.7	75%

Due to the abundant hydrogen ions in the solution, a dominant protonation reaction takes place between hydrogen ions and active sites (COO groups) [19]. Thus, the complexation between the active sites and metal ions is destroyed and the adsorbent is regenerated. However, the structure of PMA-VA and its adsorption active sites are gradually destroyed by the acid solution, leading to lower adsorption capacity after each regeneration cycle (Fig7). It was shown that PMA-VA is a good reusable adsorbent in removal of Hg(II) from their single-metal ion solution.

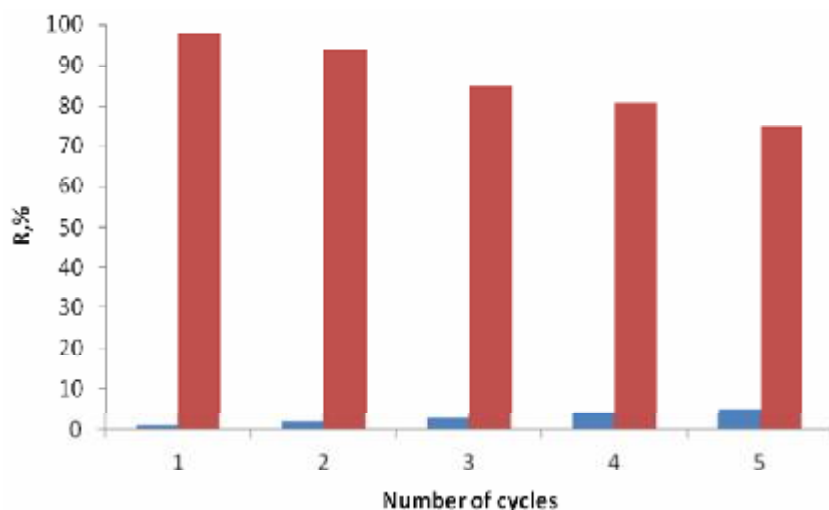


Fig.7 Regeneration efficiency of PMA-VA

4 - Conclusion

- a) Investigation the adsorption properties of PMA-VA resin towards Hg(II) in aqueous solutions, as a function of the following variables: contact time, pH solutions, initial concentration of metal ions, resin dosage ,and ionic strength .
- b) Equilibrium studies showed that, the maximum adsorption capacity of adsorbent for Hg(II) was: 0.75 mmol/g PMA-VA which shows that PMA-VA resin holds great potential to remove Hg(II) species from polluted wastewater.
- c) Regeneration of PMA-VA resin is possible by treating it with appropriate diluted mixtures of nitric acid and sodium nitrate.

Acknowledgement

The author is thankful to Prof. Dr. Hasan Kalawi for his efforts in this research, especially discussing results and rereading the manuscript.

REFERENCES

- [1]- Anirudhan, T. S., and Sreekumari, S. (2011). Adsorptive removal of heavy metal ions from industrial effluents using activated carbon derived from waste coconut buttons. *Journal of Environmental Sciences*, 23(12): 1989-1998.
- [2]- Lu, L. L., Chen, L. H., Shao, W. J., and Luo, F. (2010). Equilibrium and kinetic modeling of Pb(II) biosorption by a chemically modified orange peel containing cyanex 272. *Journal of Chemical and Engineering Data*, 55(10): 4147-4153.
- [3] Ma, N., Yang, Y., Chen, S., and Zhang, Q. (2009). Preparation of amine group - containing chelating fiber for thorough removal of mercury ions, *J. Hazard. Mater.*, 171:288-293.
- [4] Malkoc, E., and Nuhoglu, Y. (2005). Investigations of nickel (II) removal from aqueous solutions using tea factory waste *Hazard. Mater.*, 127: 120-128.
- [5] Karthika, C., and Sekar, M. (2012). Removal of Hg (II) ions from aqueous solution by Acid Acrylic Resin A Study through Adsorption isotherms Analysis. *I Res. J. Environment Sci.*1(1): 34-41.
- [6] Carmona, M., Warchol, J., A de Lucas and Rodriguez, J. (2008). Ion-exchange equilibria of Pb, Ni²⁺ and Cr²⁺ ions for H⁺ on Amberlite IR-120 resin *J. Chem. Eng.*, 53:1325 – 1331.
- [7] Lin, L. C., Li J. K and Juang, R. S. (2008). Removal of Cu(II) and Ni (II) from aqueous solutions using batch and fixed-bed ion exchange processes, *Desalination*, 225:249-259.
- [8] Lee, L. H., Kuan, Y. C and Chern, J. M. (2006). Factorial experimental design for recovering heavy metals from sludge with ion - exchange resin, *J. Hazard. Mater.*, 168:549-559.
- [9] Silva, R. M. P., Manso, J. P. H., Rodrigues, J. R. C, and Lagoa, R. J. L. (2008). A comparative study of alginate beads and an ion- exchange resin for the removal of heavy metals from a metal plating effluent, *J. Environ. Sci. Health.*43:311 1317.
- [10] Khanlarov, T., Hamdo, J. and Gambarov. D. (1994). Element-polymer complexes of maleic acid-vinylacetate copolymer with ions Eu(III), Sm(III), La(III), Ni(II) and Co(II). *J. High molecular combinations, serial B*, 36(1): 167-171.
- [11] Hamdo, J, and Deep, A. (1998). Ion Selective Electrode for Cu(II) on Copolymer Anhydride Maleic-Vinyl Acetate. *Damas. Univer. J*, 14(2):125-143.
- [12] Hamdo, J. Y. (2010). Adsorptions Of Some Heavy Metal Ions From Aqueous Solutions On A Chelating Resin Containing Carboxylic Groups, *Tichreen Univ. J.*, 32(2).
- [13] Al-kurdi, H and Hamdo. (2000). J.- The Removal of Flouride ions from aqueous solvents using a Development Ion Exchanger. *Damas. Univer. J*,16(2): 97-106.

- [14] Liu, C. F, Zhang, A. P, Li. W, Y., Yue, F. X. and Sun, R. C. (2010). Succinoylation of cellulose catalyzed with iodine in ionic liquid. *Industrial Crops and Products*, 31(2): 363-369.
- [15] Jamaluddin, A. M. and Shah, A. M. (2003). A rapid spectrophotometric method for the determination of mercury in environmental, biological, soil and plant samples using diphenylthiocarbazone, *Spectroscopy*, 17: 45–52
- [16] Razaev, Z. M. (1984). *Polymers and copolymers of maleic anhydride*. Baku, Elm, 158p.
- [17] Rengaraj, S and Kyeong, Ho. Y. and Seung-Hyeon, M. (2001). Removal of chromium from water and wastewater by ion exchange resins. *J. Haz. Mat. B*, 87: 273.
- [18] Chuh, Y. C., Mao-syong, L. and kun-rong, H. (2008). Recovery of Cu (II) and Cd(II) by a chelating resin containing aspartate groups. *J. Haz.Mat.*152: 986–993.
- [19] Ren, Y. M., Li, N., Feng, J, Luan, T. Z., Wen, Q., Li, Z. S, and Zhang, M. L. (2012). Adsorption of Pb (II) and Cu (II) from aqueous solution on magnetic porous ferrosipinel $MnFe_2O_4$. *Journal of Colloid and Interface Science*, 367: 415-421.