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# Adsorptions of Some Heavy Metal Ions from Aqueous Solutions on A Chelating Resin Containing Carboxylic Groups

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## ☐ ABSTRACT ☐

The discharge of heavy metal ions into aquatic ecosystems has become a serious matter of concern over the last few decades. These pollutants are introduced into the aquatic systems significantly as a result of various industrial operations. This paper describes the adsorption behavior of cation exchange resin maleic acid–vinyl acetate copolymer (PMA-VA) towards $Co^{2+}$,$Cu^{2+}$, $Zn^{2+}$,$Cd^{2+}$ and $Pb^{2+}$ ions and its use in purification of metal finishing wastewaters. The batch method has been employed, using solutions with concentration range from 2.0 – 14.0 mM. The adsorption behavior of five metal 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. It was found that the adsorption process depends on ion charge density and ionic diameter. Equilibrium studies showed that, the maximum adsorption capacities of adsorbent for metal ions were : 1.80, 1.72, 1.68, 1.54,1.24 mmol/g PMA-VA for $Co^{2+}$,$Cu^{2+}$, $Zn^{2+}$,$Cd^{2+}$ and $Pb^{2+}$, respectively. 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 cations of heavy metal species from polluted wastewater.

**Key words**: Adsorption, Chelating resin, maleic acid–vinyl acetate copolymer, Carboxylic Groups,$Co^{2+}$,$Cu^{2+}$, $Zn^{2+}$,$Cd^{2+}$ and $Pb^{2+}$ ions

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# إمتزاز بعض أيونات المعادن الثقيلة من المحاليل المائية باستخدام ريزين مخلبي ذي مجموعات وظيفية كربوكسيلية

**الدكتور جمال يونس حمدو**[*]

(تاريخ الإيداع 5 / 10 / 2009. قُبِل للنشر في 1 / 2 /2010)

## ملخّص

أضحت في العقود الأخيرة، عملية رمي مخلفات النشاطات الصناعية المختلفة، لاسيما أيونات العناصر الثقيلة، في المنظومات المائية المختلفة، مشكلة بيئية عالمية خطرة. تعرض هذه الورقة البحثية نتائج قياسات إمتزاز الأيونات $Co^{2+}$ و$Cu^{2+}$ و $Zn^{2+}$ و $Cd^{2+}$ و$Pb^{2+}$ من المحاليل المائية باستخدام البولمر المشترك حمض المالئيك– أستات الفينيل PMA-VA، بهدف إظهار إمكانية استخدام هذا البولمر(الريزين) في معالجة تلوث المياه الطبيعية بأيونات العناصر الثقيلة. استخدمت في هذه الدراسة طريقة الدفعات( batch method )، باستخدام محاليل تتراوح تراكيزها بين 2.0 و14.0 ميلي مول/ليتر. درست مختلف العوامل التي تؤثر في السعة الإمتزازية للريزين مثل زمن التوازن والتركيز الابتدائي للأيون المدروس وكمية الريزين وحموضة الوسط والقوة الأيونية. وجد أن عملية الإمتزاز تعتمد على كثافة الشحنة الأيونية ونصف القطر الأيوني . كانت السعة الإمتزازية العظمى للريزين تجاه الأيونات $Co^{2+}$ و$Cu^{2+}$ و$Zn^{2+}$ و $Cd^{2+}$ و$Pb^{2+}$ تساوي 1.80و1.72 و 1.68 و1.54و1.24 ميلي مول/ غ من الريزين PMA-VA. درست أيضاً إمكانية الاستخدام المتكرر للريزين بإعادة تنشيطه بمعالجته بمحلول مخفف من حمض النتريك ونترات الصوديوم. يستدل من نتائج الدراسة على تمتع الريزين بإمكانية كبيرة في نزع أيونات العناصر الثقيلة من المياه الصناعية الملوثة.

**الكلمات المفتاحية:** الإمتزاز، الريزينات المخلبية، البولمير المشترك حمض المالئيك– أستات الفينيل، المجموعات الوظيفية الكربوكسيلية، الأيونات $Co^{2+}$ و$Cu^{2}$ و $Zn^{2+}$و $Cd^{2+}$ و$Pb^{2}$ .

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## Introduction:

Pure water progressively becomes a rare resource on earth, because of vast human activities that release increasing amounts of soluble and nonsoluble chemical species into natural water, that are not appropriately removed before returning water to the environment. Among the number of polluting species at issue are the ions of heavy metals [1]. Heavy metal pollution occurs in many industrial wastewater such as those produced by metal plating facilities, mining operations, battery manufacturing process, production of paints and pigments, and glass production industry[2].

Different techniques and processes are currently used to reduce heavy metal concentrations in wastewater. Membrane processes [3], advanced oxidation processes [4], chemical and electrochemical techniques [5,6], and adsorption procedures [7,8] are the most widely used techniques for metals removing from industrial effluents. Many researches concentrated on metal ion recovery using chelating polymers as ion exchangers, because they are reusable, easy handling and have higher adsorption capacities with efficiencies as well as high selectivity to some metal ions [9,10].

Ion exchange technique is widely used method for the separation and pre-concentration of inorganic ions. In ion exchange, positively and negatively charged ions from an aqueous solution replace dissimilar ions of the same charge initially present in the solid. Cation-exchange resins generally contain bound sulfonic acid groups; carboxylic, phosphonic, and so on. Certain general rules for cation exchange are: (i) the exchanger prefers ions of high charge, (ii) ions of small hydrate volume are preferred and (iii) ions, which interact strongly with the functional groups of the exchangers are preferred [11–18].

It is well known in the literature that, carboxylic functional groups can form metallic complexes and behave as ion exchangers. These properties provide a wide range of applications to the copolymer PMA-VA, which contains in its structure carboxylic groups. This copolymers in its soluble form, can form stable complexes with most of heavy metal ions, which makes it rather useful as masking agent for trivalent charged cations in their spectrophotometric interferences with bivalence cations[19].Also researchers used the soluble form of this copolymer for preparing selective membrane , which can be used in preparing ion selective electrode for $Cu^{2+}$[20]. In addition, the copolymer PMA-VA was used as ion exchanger for 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 [21].

## The Aim of The Work:

This work aims to evaluate the possibility of employing insoluble form of maleic acid–vinyl acetate copolymers (PMA-VA) in removal of some heavy metal ion from aqueous solutions.

## .Materials and Methods:

### 1 -Apparatus and Reagents:

A spectro123-Labomed/USA was used for the spectrophotometric determination of metal ions in solutions. The pH measurements were made with Orion pH meter having a glass electrode.

All chemicals used were of analytical grade, and distilled water was used throughout the study. A stock solutions of $Cu^{2+}$,$Cd^{2+}$,$Pb^{2+}$,$Zn^{2+}$,$Co^{2+}$ at a concentration of $1.0 \times 10^{-2}$ M each, were prepared by dissolving copper(II) nitrate, cadmium(II) nitrate, lead(II) nitrate ,zinc nitrate and Cobalt(II) nitrate in 0.01M nitric acid. Working standard solutions were prepared daily by appropriate dilution with distilled water. Lead stock solution was prepared by dissolving $Pb(NO_3)_2$ in distilled water and filtering through a suitable membrane. The concentration of above mentioned ions were determined separately by spectrophotometric method, using 4-2(pyridel azo)resorcinol (PAR ) as spectrophotometric reagent[22].The solutions were standardized and working solutions of lower concentration were obtained by dilution. $NH_3$–HAc Buffer solutions were prepared by mixing 200.0 ml of 1.0 M acetic acid solution and 200.0 ml of 1.0 M ammonia solution, then, pH adjusted to a suitable value by adding acetic acid or ammonia. The insoluble PMA-VA copolymers was prepared and purified in the laboratory as described in the literature [21] 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 .

**2- Adsorption Studies:**

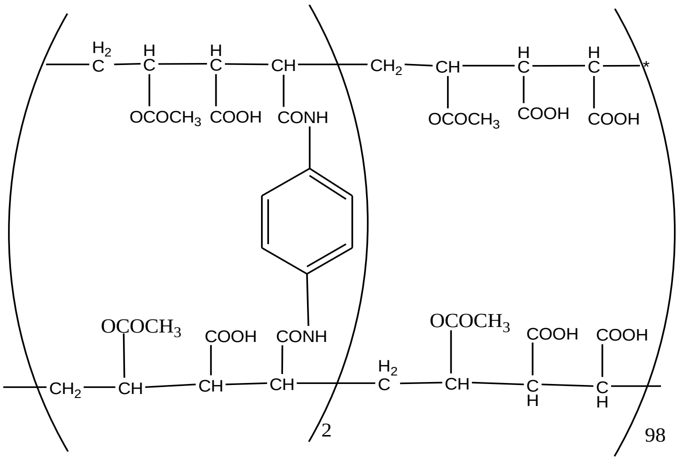
All the adsorption studies were conducted by mixing 100.0 mg of PMA-VA and 25.0 ml of metal ions in a flask with a magnetic stirrer at about 120 rpm and at 25.0±0.2 °C. The ionic strength of the metal ion solutions were controlled by adding $NaNO_3$.The pH value of each metal ion solution was adjusted with $NH_3$–HAc buffer. 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 spectrophotometically using PAR as spectrophotometric reagent. The adsorption capacities *Q* (mmol/g PMA-VA) were calculated by using the following expression:

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

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

## Results and discussion:

Maleic anhydride is well known to form the alternating copolymers with different monomers [23]. 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. The properties of the resins are given in Table 1.



Maleic acid -vinyl acetate copolymer
(PMA-VA)

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

**Table 1. Physical and chemical properties of the cation exchange resin PMA-VA**

| Properties | Description or values |
|---|---|
| Type | Weak acid cation exchanger acetic acid. |
| Active groups | Carboxylic groups. |
| Matrix | Gel(microporous)- maleic acid–vinyl acetate copolymer |
| Ionic forms as shipped | $H^+$ |
| Physical form | Spherical beads |
| Mean particle size (μm) | 60-140 |
| Effective pH range | > 4 |
| Total exchange capacity($H^+$ form) mmol/g dry resin | Depends on the type of ion |
| Specific gravity | 1.14 |

### 1- **Time-dependent Adsorption Behavior:**

To study the capacity of the PMA-VA resin for adsorption of heavy metal ions, samples of synthetically polluted water were prepared by adding the specific quantity of pollutants such as $Cu^{2+}$,$Cd^{2+}$,$Pb^{2+}$,$Zn^{2+}$,and $Co^{2+}$. The variation of adsorption capacities towards each of these ions as a function of contact time is shown in fig.2. From this figure, it is clear that the adsorption of $Cu^{2+}$,$Cd^{2+}$,$Pb^{2+}$,$Zn^{2+}$,and $Co^{2+}$ increases strongly during the first 25 min and tends toward equilibrium at approximately 60 min. Accordingly, all other adsorption studies in this article were examined during the first 65 min to confirm the complete equilibria between PMA-VA and metal ions. The blank tests for the adsorptions of $Co^{2+}$,$Cu^{2+}$, $Zn^{2+}$,$Cd^{2+}$ and $Pb^{2+}$, by PMA-VA were also performed for 65 min and found to be less than 0.001 mmol/g PMA-VA. The equilibrium adsorption capacities were 1.80, 1.72, 1.68, 1.54 and 1.24 mmol/g for $Co^{2+}$,$Cu^{2+}$, $Zn^{2+}$,$Cd^{2+}$ and $Pb^{2+}$ respectively. Numerous researchers [11,13,14] believed that the resins containing carboxylate, sulfonate or phosphate anions preferred cations of high charge and small hydrated volume. The charge density of $Co^{2+}$ is greater than that of $Cu^{2+}$, $Zn^{2+}$,$Cd^{2+}$ and $Pb^{2+}$ because the ionic radius order is as follows: $Co^{2+}$ (0.78°A)< $Cu^{2+}$ ($0.80A^0$)< $Zn^{2+}$ (0.83A°)< $Cd^{2+}$($99A^0$)<<$Pb^{2+}$($1.26A^0$) [24].As PMA-VA adsorbing metal ions, the polymer chains shrink, because the fraction of the free chelating site (hydrophilic region) decreases. Thus, metal ions are difficult to diffuse toward the free chelating sites and the adsorption process will reach equilibrium. However, $Co^{2+}$,$Cu^{2+}$,and $Zn^{2+}$ possess small ionic radii compared with $Cd^{2+}$ and $Pb^{2+}$, subsequently have large charge/radius ratio and that can still diffuse toward the adsorption sites. That is, the equilibrium adsorption capacity of $Co^{2+}$,$Cu^{2+}$,and $Zn^{2+}$ are greater than that of $Cd^{2+}$ and $Pb^{2+}$.

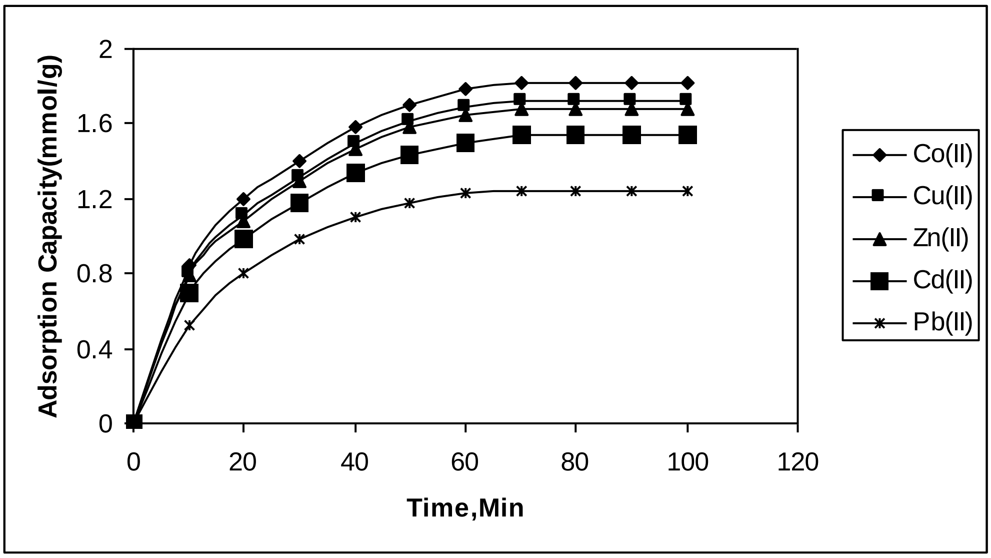


**Fig. 2. Effect of adsorption time on the adsorption capacities of $Cu^{2+}$,$Cd^{2+}$,$Pb^{2+}$,$Zn^{2+}$,and $Co^{2+}$ under noncompetitive condition at 25.0±0.2 $^{0}$C, pH5 (initial concentration of metal ion =7.30 mM).**

It's assumed that, adsorption of heavy metal ions on proposed resin takes place according to two mechanisms: ionic exchange between hydrogen of carboxylic groups of resin and ions 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 rabid 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. Fig.3 shows the interaction between PMA-VA and metal ion $M^{2+}$.

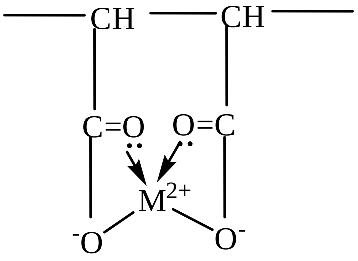


**Fig.3. the interaction between PMA-VA and a metal ion.**

## 2- Effect of resin amount:

Adsorption of $Co^{2+}$,$Cu^{2+}$, $Zn^{2+}$,$Cd^{2+}$ and $Pb^{2+}$ ions from a given solution (initial concentration of : $Co^{2+}$, 7.30 mM, $Pb^{2+}$= 5.00 mM and pH5) was measured with different amount of the resin in the range of 25.0 - 200.0 mg and equilibrated for 65 min . All experiments were carried out at the same conditions. As an example, Fig.4 shows variation of adsorption percentage of $Co^{2+}$ and $Pb^{2+}$ with resin dosage. It was found that the amount of adsorbed metals increased with increasing amount of the resin up to 100.0 mg. This value was taken as the optimum amount for other trials. This result was expected because for a fixed initial metal concentration, increasing adsorbent amount provides greater surface area and adsorption sites [25].

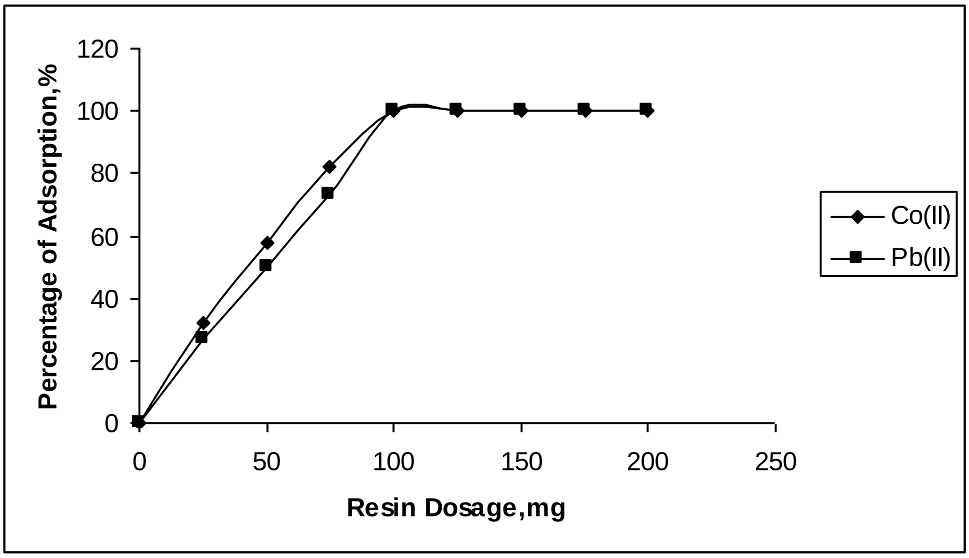


**Fig. 4. Effect of resin dosage on the ion exchange of $Co^{2+}$ and $Pb^{2+}$on PMA-VA resin (initial concentration of : $Co^{2+}$, 7.30 mM, $Pb^{2+}$= 5.00 mM and amount of resin,25-200 mg; volume of sorption medium, 25 ml, temperature, 25±2$^0$C; stirring rate, 180 rpm; pH5).**

## 3- Effect of initial ion concentration on Adsorption:

The influence of the initial concentrations of $Co^{2+}$ and $Pb^{2+}$ ions on adsorption capacities are presented as an example in Fig. 5. The adsorption capacities increased first with increasing initial concentration of metal ion, then reached a plateau value. When the initial concentrations of metal ion were less than 7 mM, the quantity of adsorption sites in PMA-VA were vastly more than the amount of metal ion in tested solution. After the adsorption process, the metal ions were almost adsorbed by PMA-VA and the residue concentrations of metal ion in the solution were negligible. Thus, the adsorption capacities of $Co^{2+}$, $Cu^{2+}$, and $Zn^{2+}$, were closed. These high adsorption efficiencies were attributed to the hydrophilic nature of carboxylate ($–COO^-$) 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[26]. As the concentrations of metal ion increased, PMA-VA adsorbed more metal ions and the polymer chains shrunk. $Cd^{2+}$ and $Pb^{2+}$ would be hard to diffuse toward the free chelating sites within PMA-VA but $Co^{2+}$,$Cu^{2+}$, and $Zn^{2+}$ could diffuse to the free sites. This is why the curves of adsorption capacity diverge at high concentrations of metal ions.

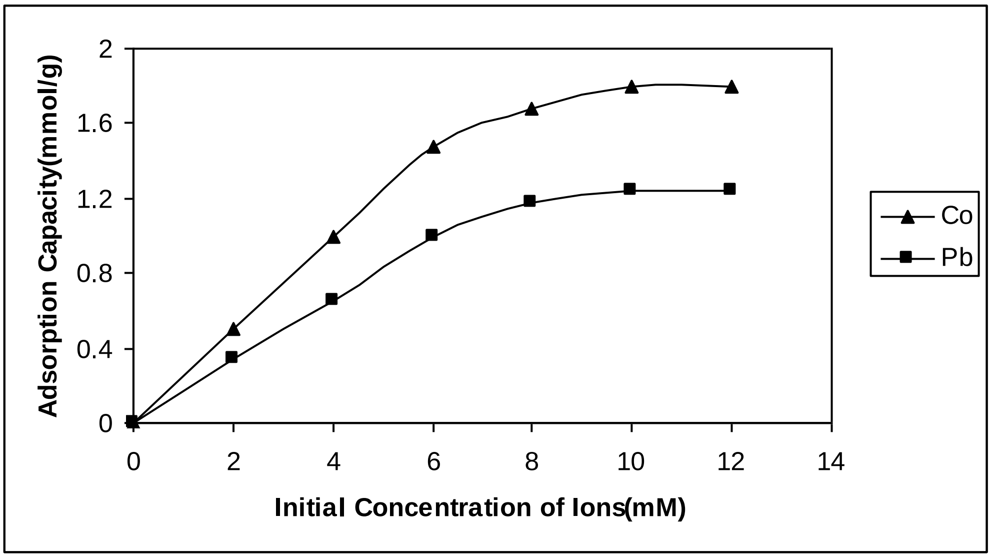


**Fig. 5. The influence of the initial concentrations of metal ions on the equilibrium adsorption capacities by PMA-VA at 25 $^0$C, pH 5 (adsorption time = 65 min).**

### 4- Effect of pH on Adsorption:

Fig. 6 shows the effect of the solution pH on the adsorptions of $Co^{2+}$ and $Pb^{2+}$ by PMA-VA,. The pH in a range of 1–5 was chosen to avoid the precipitations of hydroxides as $Co(OH)_2$ and $Pb(OH)_2$. The adsorption capacities increased with an increase in solution pH. At low pH values, high concentrations of $H^+$ can react with carboxylate ions ($-COO^-$) within PMA-VA giving protonated forms, which induces an electrostatic repulsion of metal ions. Therefore, competition arises between $H^+$ and metal ions for adsorption sites and decreases the adsorption capacity..

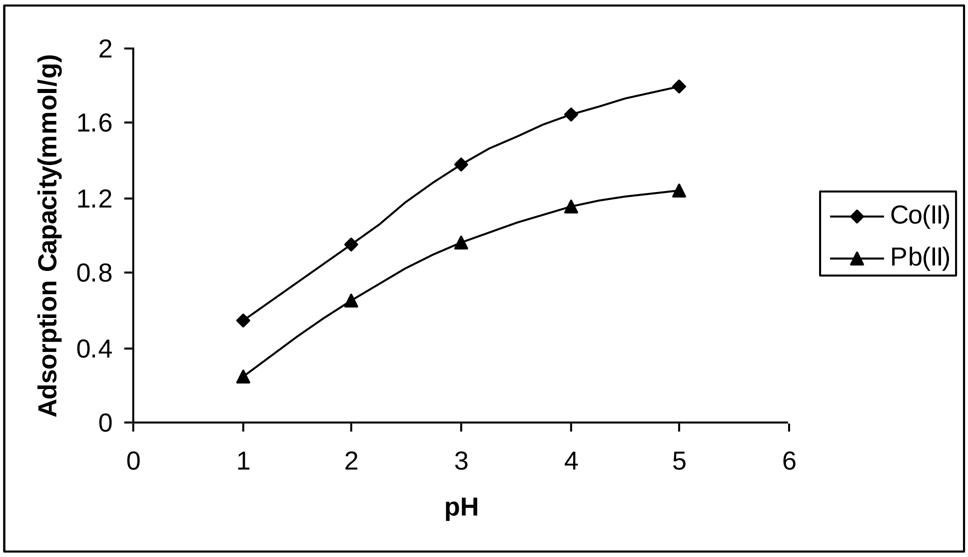


**Fig. 6. Effect of the pH on the adsorptions capacity of metal ions by PMA-VA at 25$^0$C (initial concentration of metal ion = 7.30 mM; adsorption time = 65 min).**

## 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 heavy metal ions. Fig. 7 shows the adsorptions of $Co^{2+}$,$Cu^{2+}$, $Zn^{2+}$,$Cd^{2+}$ and $Pb^{2+}$ by PMA-VA in the presence of 0–1.0 mol/l of $NaNO_3$. Obviously, as the concentrations of $NaNO_3$ in ion solutions increased from 0.1M-0.5 M , the adsorptions of $Co^{2+}$,$Cu^{2+}$, $Zn^{2+}$,$Cd^{2+}$ and $Pb^{2+}$ decreased negligently in the case of first three ions and significantly in the case of the residual ions within the mentioned concentrations of $NaNO_3$. As the concentration of $NaNO_3$ in solution increased more than 0.50 M, negative effect on the adsorption proceeds for all ions, but the considerable effect observed for last two ions. . As stated above, the charge density of $Co^{2+}$,$Cu^{2+}$ and $Zn^{2+}$, is greater than that of $Cd^{2+}$ and $Pb^{2+}$. The attraction of the carboxylic group for $Co^{2+}$,$Cu^{2+}$ and $Zn^{2+}$, is stronger than that for $Cd^{2+}$ and $Pb^{2+}$. Therefore, adsorption of $Co^{2+}$,$Cu^{2+}$ and $Zn^{2+}$, are affected slightly in the presence of $NaNO_3$ but the uptake of $Cd^{2+}$ and $Pb^{2+}$ decreases significantly in the same conditions.

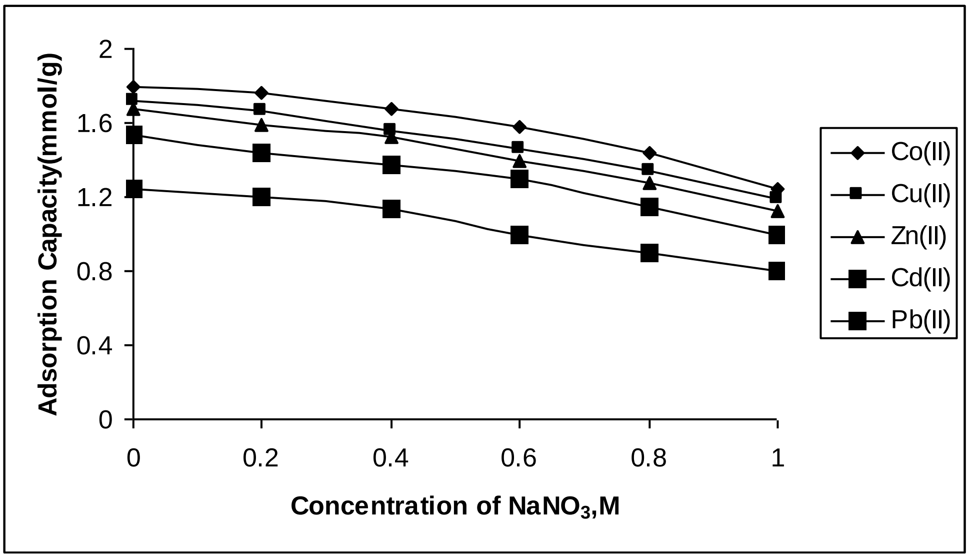


**Fig. 7. The adsorptions of metal ions by PMA-VA in the presence of $NaNO_3$ at 25 $^0$C, pH5 (initial concentration of metal ion = 7.30 mM; adsorption time = 65 min).**

## 6- Desorption and reuse:

Desorption of metal ions from PMA-VA –metal ion was carried out using 0.20 M $HNO_3$+ 0.60 M $NaNO_3$ solution at 25 $^0$C. As stated previously, no adsorption was observed at pH< 1, demonstrating that, the concentration of hydronium ions in this condition > 0.10 M, which inhibits the adsorptions of metal ions. The desorption process reached equilibrium at about 22 min for all ions and the desorption ratios were approximately 99% for all studied ions . Table 2 displays the adsorptions of $Co^{2+}$,$Cu^{2+}$, $Zn^{2+}$,$Cd^{2+}$ and $Pb^{2+}$ after 5 recycles of consecutive adsorption–desorption procedures. The results are taken as the mean of three values and RSDs doesn't exceed 3.5% for all adsorption-desorption operations. The adsorption capacities showed a slight decrease. The results in the tab2. show that PMA-VA is a good reusable adsorbent in removal of $Co^{2+}$,$Cu^{2+}$, $Zn^{2+}$,$Cd^{2+}$ and $Pb^{2+}$from their single-metal ion solutions. 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 (–COOH) or salt (-COONa).

**Table2.The adsorption capacities of PMA-VA after repeated adsorption–desorption operations at 25 °C, pH 5. Concentration of metal ion = 7.30 mM; Adsorption time = 65 min.**

| Metal ion | Adsorption capacity (mmol/g PMA-VA) | | | |
|---|---|---|---|---|
| | Recycle 0 | Recycle 1 | Recycle3 | Recycle 5 |
| $Co^{2+}$ | 1.80 | 1.78 | 1.74 | 1.71 |
| $Cu^{2+}$ | 1.72 | 1.67 | 1.65 | 1.62 |
| $Zn^{2+}$ | 1.68 | 1.64 | 1.61 | 1.59 |
| $Cd^{2+}$ | 1.54 | 1.51 | 1.48 | 1.47 |
| $Pb^{2+}$ | 1.24 | 1.22 | 1.19 | 1.17 |

## Conclusion:

**a)** Investigation the adsorption properties of PMA-VA resin towards $Co^{2+}$,$Cu^{2+}$, $Zn^{2+}$,$Cd^{2+}$ and $Pb^{2+}$ 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) It was found that the adsorption process depends on ion charge density and ionic diameter.

**c)** Equilibrium studies showed that, the maximum adsorption capacities of adsorbent for metal ions were : 1.80, 1.72, 1.68, 1.54,1.24 mmol/g PMA-VA for $Co^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$ and $Pb^{2+}$, respectively which shows that PMA-VA resin holds great potential to remove cations of heavy metal species from polluted wastewater.

d) Regeneration of PMA-VA resin is possible by treating it with appropriate diluted mixtures of nitric acid and sodium nitrate.

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