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Al-Khriet Agricultural Waste Adsorbent, for Removal Lead and Cadmium Ion from Aqueous Solutions

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Abstract

The availability of low- cost adsorbent namely Al-Khriet (a substance found in the legs of Typha Domingensis) as an agricultural waste material, for the removal of lead and cadmium from aqueous solution was investigated. In the batch tests experimental parameters were studied, including adsorbent dosage between (0.2-1) g, initial metal ions concentration between (50-200) ppm (single and binary) and contact time (1/2-6) h. The removal percentage of each ion onto Al-Khriet reached equilibrium in about 4 hours. The highest adsorption capacity was for lead (96%) while for cadmium it was (90%) with 50 ppm ions concentration, 1 g dosage of adsorbent and pH 5.5. Adsorption capacity in the binary mixture were reduce at about 8% for lead and 12 % for cadmium, which was attributed to competitive adsorption. The adsorption parameters were analyzed using both the Freundlich and Langmuir. Al-Khriet was best fitted by the Freundlich isotherm comparing with Langmuir model, and the rate constant was found to be 1.305 and 0.621 $((mg/g)(L/mg)^{1/n})$ for lead and cadmium respectively , while the kinetic of adsorption obeyed a second order rate equation and the rate constants were found to be (0.0161) for lead and (0.0125) $mg.g^{-1}.min^{-1}$ for cadmium.

Keywords: *Agricultural waste adsorbent**,** Biosorption, heavy metal ions, isotherm kinetic model**.***

1. Introduction

The rapid progress in industrial technology and war remnants in Iraq causes an increase in the level of toxic ions discharged into the waste water and these metals are harmful to the human and aquatic lives. Many countries pay attention to this global issue and they devote concentrated efforts to solve this environmental problem (Abdel-Ghani et al., 2009).

Lead is one of the very dangerous heavy metals, which causes many dysfunctions in all human beings. In children, excess amounts of this metal would probably lead to a decrease in their IQ score, and an impairment of learning, hearing, physical growth, the circulating system, the reproductive system, nervous system especially the brain, kidney functions and some mental disease such as dementia, depression, madness, as well as problems in metabolism system.,e.g., deficiency of vitamin D, also increasing level of this toxic metal may lead to death (Okoye et al., 2010, Okoro and Ejike, 2007). Lead as (Pb^{+2}) has a huge efficiency to the thio (-SH) and (PO_4) containing enzymes and other dangerous molecules which in turn affecting the permeability of kidney, liver and brain cells by inhibiting the synthesis of heams unit, leading to retardation or break down of these organs function (Ademoroti, 1996).

Cadmium is another of heavy metals with a high toxicity. Accumulation of cadmium in the body results in, diarrhea, muscular cramps, nausea, erythritis, problem in the vision, chronic pulmonary disease (CPD), and cardio vascular disease (CVD). The world health organization (WHO) gave the recommended standards of drinking water which is 0.005mg Cd/L and 0.001 mg Pb/L (Munther I. et al.,2010). While in Iraq in the trocar of Al-Eshaki because of the effect of Al-Somood company for steel industry and power plant in the south of Baghdad, the level of toxic metals (Cd^{+2},Pb^{+2}) exceeded the allowed limit for example, the concentration of cadmium ion was 8 mg/L and the concentration of lead ion was 10 mg/L which was must higher than the permissible limits for drinking water.

Many techniques such as ion exchange, precipitation, adsorption, flocculation, advance oxidation and membrane process have been used for the removal of toxic metal ions (Sheela et al., 2012, Mohamad et al.,2012). The reason behind our using the absorption technique is that it is a very economical process especially when using a locally available adsorbent (Saad Al-Jlil, 2010). The essential benefits of this absorption process for environmental pollution are: the low cost, simple design easy operation as well as no effect of toxic substance, when comparing to other biological treatment process (Yahia, 2006, Hameed et al., 2009).

This research investigated the possibilities for using cheap wasted material, locally available in Iraq namely Al-Khriet which is found as a powder in the legs of Typha Domingesis as potential adsorbent. The Presence of this plant in industrial waste water indicates that it resists the pollutants. The effect of various parameters including the adsorbent dosage initial of metal ion concentration (single and binary) and contact time were studied onto Al-Khriet powder for removal lead and cadmium ion from aqueous solution. By reviewing other literature surveys, it is obvious that a few of them were performed on the contamination levels of different heavy metals in the waste water in Iraq.

2. Material and Methods

2.1. Material

Al-Khriet was collected from marshes in the south of Iraq. First it was washed with deionized water to remove the suspended particle and then dried in the air for two days before drying in an oven at 110°C for 24 hours, Finally Al-Khriet powder was stored in discator.

2.2. Experimental Work

Different concentrations of Cd^{+2},Pb^{+2} aqueous solution were prepared from the stock of 500 mg/L solution prepared by dissolving agent grade $Pb(NO_3)_2.2H_2O$ and $Cd(NO_3)_2$ in dionized water, the properties of these compound were shown in Table 1. Adsorption was performed in a batch experiment. The equilibrium isotherms were determined by mixing 0.5gm of Al-Khriet with 25 ml of Cd^{+2},Pb^{+2} solutions in a conical flask at different concentration (50,100,150 and 200) mg/L. Flasks were shaken in a shaker (type B,Baun Karlkob) for 4 h at room temperature. It was noticed that the adsorbed metals ions of adsorbent system reached to equilibrium after 4 h. This phenomenon was clearly seen in a series of experiments of different time intervals which showed that the adsorption process reached equilibrium after 4 h. Solution and adsorbents were separated by filtering through a filter paper. The concentration of the solute in solution was determined by using atomic absorption spectrophotomeric (type Perkin-Elmer-5000, USA) . The adsorbed amount was calculated by the following equation:

$$q_e = \frac{V(C_0 - C_e)}{w} \qquad \ldots(1)$$

Where q_e (mg/g) is the amount adsorbed at equilibrium, V (L) is the volume of solution, C_0, C_e (mg/L) is the initial and equilibrium concentration, w (g) is the amount of adsorbent. The adsorption kinetic was analyzed by adding 0.5 g of Al-Khriet to 25 ml of 50 mg/L of Cd^{+2}, Pb^{+2} solutions. The samples were shaken and examined at different time intervals. The effect of adsorbent dosage and initial concentration of the feed solution were also studied by using different amount of adsorbent (0.2-1) gm for initial concentration of (50-200) mg/L (single and binary). The pH value for cadmium and lead were 5.5 before and after mixing with adsorbent. 0.1M of NaOH and HCl were used for pH adjustment to fix the pH value in all experiments.

Table 1,
Physical Properties of Adsorbate.

Adsorbate	Lead Nitrate	Cadmium Nitrate
Molecular weight (g/mol)	367.2098	236.4208
Water solubility (g/ 100ml $_{H2O}$) at 20°C	52	136

3. Results and Discussion

The removal efficiency was calculated by the equation below

$$\text{Removal efficiency}(R) = \frac{C_0 - C_f}{C_0} * 100 \qquad \ldots(2)$$

Where C_0 and C_f are the initial and final ions concentrations, respectively.

3.1. Effect of Contact Time

As shown in Fig.1, the percent removal of lead ion and cadmium ion by adsorption onto Al-Khriet increases with contact time and attain equilibrium in about 4 h. Removal efficiency equal to (94.6%) and (85.9%) for lead and cadmium ion respectively at pH 5.5 and of 50 ppm ions concentration and 0.5 gm of adsorbent in 4 h. The result indicates that the rate of sorption of both ions on Al-Khriet was fast because of a largest amount of Cd^{+2},Pb^{+2} attached to the sorbents within 1 h of adsorption. Similar results were reported by Mahvi et al.,(2007), Ajmal et al.,(2003) and Madhava et al., (2008). This behavior suggests that the initial stage, sorption takes place rapidly on the external surface of the Al-khriet followed by a slower internal diffusion process, which may be the rate determine step. The reason behind our studying this part because the equilibrium time is one of the parameters for economical waste water treatment plant application. These observation agree well with the investigation by Hameed et al., (2009). Lead was found to adsorb more than cadmium, that is due to its different affinities of two ion for the reactive functional groups located on the surface of Al-Khriet powder.

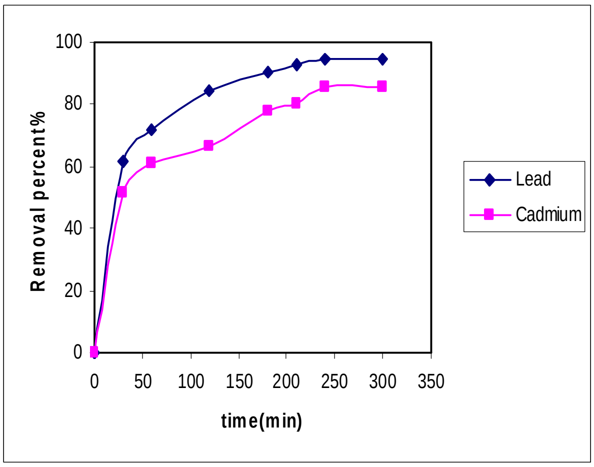

Fig. 1. Effect of Time on the Removal Efficiency using Al-Khriet as Adsorbent, Biomass Dosage 0.5 g, pH 5.5, 250 rpm , Cd^{+2} , Pd^{+2} Concentration 50 ppm.

3.2. The Effect of Al-Khriet Dose on Ions Adsorption

The relation between Al-Khriet dose and % removal efficiency of Cd^{+2} and Pb^{+2} are shown in Figs. 2 and 3. The experiments were carried out at pH 5.5 and fixed Cd^{+2} and Pb^{+2} initial concentrations for both single and binary of 50 ppm solution on Al-Khriet. As can be depicted from these figures, when Al-Khriet dose increased, the uptake of both ion decreased and the percent removal increased for both single and binary solution due to the great possibility of exchangeable sites or surface area. It is appearance that by increasing the dosage from (0.2-1) g, the percent removal increased from (92% to 96%) for lead and from (83% to 90%) for cadmium as shown in Fig.2. Figure 3. shows that the adsorption curve for two solute together. In the binary solution adsorption percent removal of Pb^{+2} and Cd^{+2} were 88%, 79% with 1 g dosage and 50 ppm ion concentration. This indicates that the adsorption capacities of the adsorbent observed in binary mixture batch experiments were lower (about 8% for Pb and 12% for Cd) than that observed in a single solute, which was attributed to competitive adsorption. Competitive adsorption results from the available adsorption sites existing on the surface of the adsorbent when present in a multi-component metal ion aqueous solution. It was found that the removal efficiency of Al-Khriet for Pb^{+2} is grater than Cd^{+2}. It can be clearly seen from table 1 that lead nitrate is less soluble than cadmium nitrate which attribute to their molecular weight, duo to the fact that the higher molecular weight, the lower solubility in a water is similar trend was reported by Riaz Qadeer (2002). This behavior might be also attributed to the molecular size. Lead ion has the smaller molecule than cadmium ion, thus it might be visible for on particular pore hold more lead ions molecules than cadmium ions molecules. The decreasing trend in adsorbed phase concentration for cadmium ion is due to the less availability of sites on the Al-Khriet because of the competitive effect of lead ions.

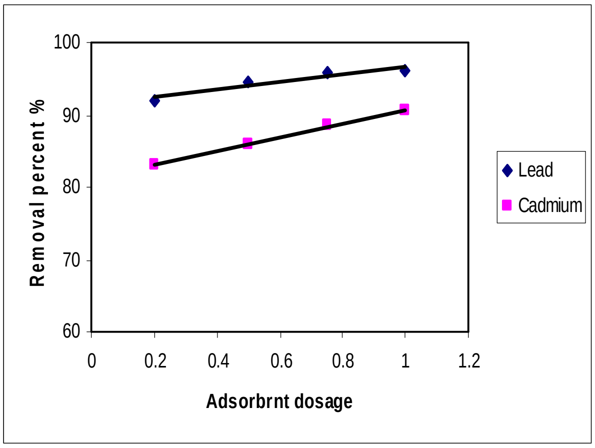

Fig. 2. Effect of Adsorbent Dosage on the Percent Removal for Single of Cd^{+2}, Pb^{+2} by Al-Khriet , Contact Time 4 h, Initial Concentration for Both Ion 50ppm.

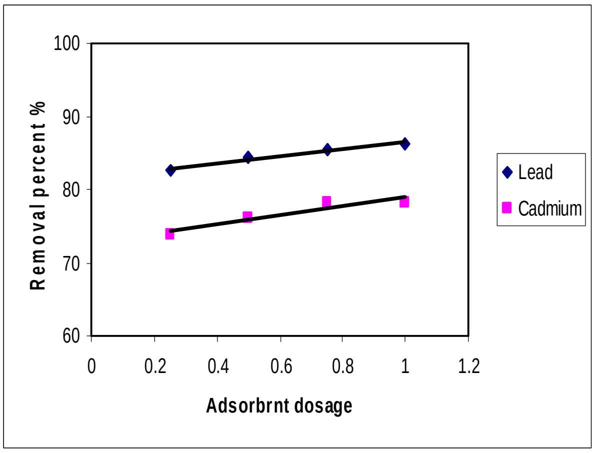

Fig. 3. Effect of Adsorbent Dosage on Percent Removal for Binary System of Cd^{+2}, Pb^{+2}, using Initial Concentration for Each Ion 50 ppm.

3.3. Effect of Initial Cd^{+2}, Pb^{+2} Ions Concentration

Figure 4 showed the relation between the percent removal efficiency and the initial ions concentration of Cd^{+2} and Pb^{+2}, as the initial ions concentration increase the percent removal decreases. That is because at higher concentration, number of heavy metals were relatively higher in comparison with the availability of adsorbent sites. These observation agree well with the investigation reported by Sulaymon et al., (Sulaymon et al.,2010) .

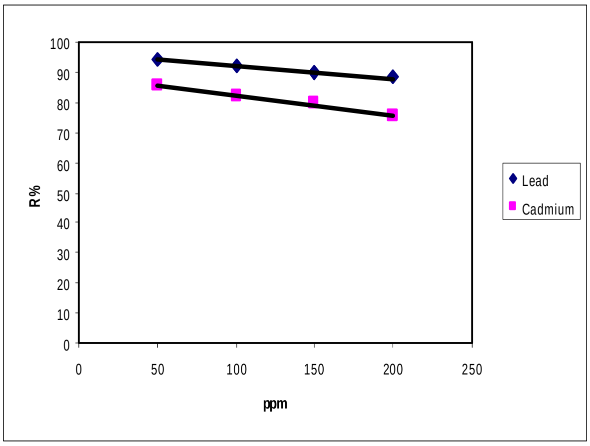

Fig. 4. Removal of Cd^{+2}, Pb^{+2} Ion using Different Concentration of Ions.

3.4. Adsorption Kinetic Model

The pseudo first order model (PFOM) (Augustin and Emmanual,2011) is given by the following equation

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \ldots(3)$$

The pseudo second order model (PSOM) (Augustin and Emmanual,2011) is given by the following equation

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

Where q_e is the amount of ions adsorbed at equilibrium ($mg.g^{-1}$), q_t is the amount ions adsorbed at time t in ($mg.g^{-1}$), k_1 (min^{-1}) and k_2 (g/(mg.min)) are the rate constants of PFOM and PSOM respectively.
The PFOM and PSOM plots shown in Fig. 5 and 6.

k_1 and k_2 for Cd^{+2}, Pb^{+2} as well as correlation coefficient obtained are presented in table 2. It can be found out that the obtained correlation coefficient for PSOM were greater than for PFOM. These suggest that the adsorption system is the second order model based on assumption that the both sorbate (Pb,Cd) and Al-Khriet are involved in a rate determining step, which may be a chemical sorption rather than diffusion. (Ho and Mckay, 1998).

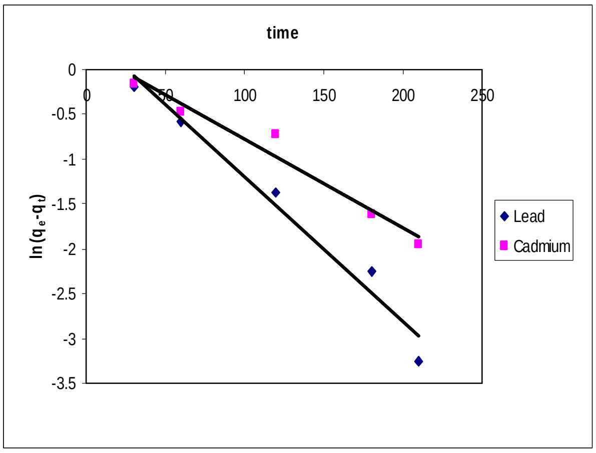

Fig. 5. PFOM Plots for Cd^{+2}, Pb^{+2}.

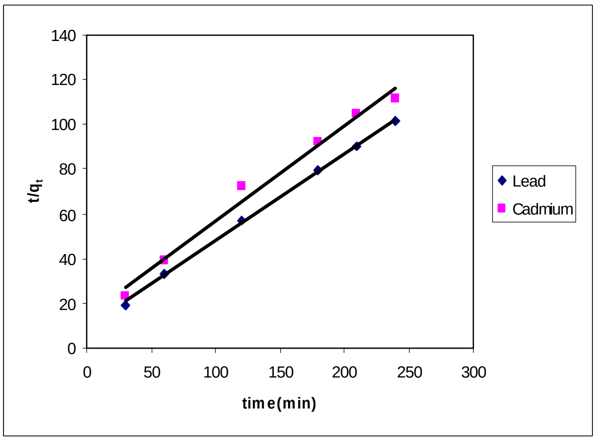

Fig. 6. PSOM Plots for Cd^{+2}, Pb^{+2}.

Table 2,
The Rate Constant and Correlation Coefficient for Pseudo First and Second Order for Both Ions.

Kinetic model	Parameters	Pb^{+2}	Cd^{+2}
PFOM	$k_1(min^{-1})$	0.0161	0.0099
	q_e (mg/g)	1.50	1.22
	R_1^2	0.9718	0.9613
PSOM	k_2 ($mg.g^{-1}.min^{-1}$)	0.0161	0.0125
	q_e (mg/g)	2.582	2.353
	R_1^2	0.9991	0.9866

3.5. Equilibrium Isotherms

The equilibrium isotherm display a nonlinear dependence on the equilibrium concentration. The obtained adsorption data were analyzed using Freundlich and Langmuir (Ajay et al., 2010) isotherms according to the following equation:

$$q_e = kC_e^{\frac{1}{n}} \qquad \text{...(9) Freundlich}$$

$$q_e = \frac{q_m bC_e}{1+bC_e} \qquad \text{...(10) Langmuir}$$

Equations 9 and 10 can be written in linear form as given below respectively

$$\ln q_e = \ln k_f + \frac{1}{n}\ln C_e \qquad \text{...(11)}$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \qquad \text{...(12)}$$

Where q_e and C_e are the equilibrium concentration of lead and cadmium in adsorbed and liquid phase in mg/g and mg/L , respectively , k_f and n are the Freundlich constants which can be calculated from the slope and intercepted of the linear plot with $\ln q_e$ vs. $\ln C_e$.

q_m and b are Langmuir constants which can be calculated from the intercept and slope of the linear plot C_e/q_e vs. C_e.

The Freundlich and Langmuir isotherms are shown graphically in Figs. 7 and 8. The fitted constant for two models are tabulated in table (3). Table (3) indicate the Freundlich model provides the best fit as judged by its correlation coefficient for Pb^{+2} and Cd^{+2}. The n value of Freundlich model between 1 and 10, indicates good adsorption efficiency (Treybal,1980). This demonstrate that the developed adsorbent has good adsorption efficiency for Pb^{+2},Cd^{+2} removal.

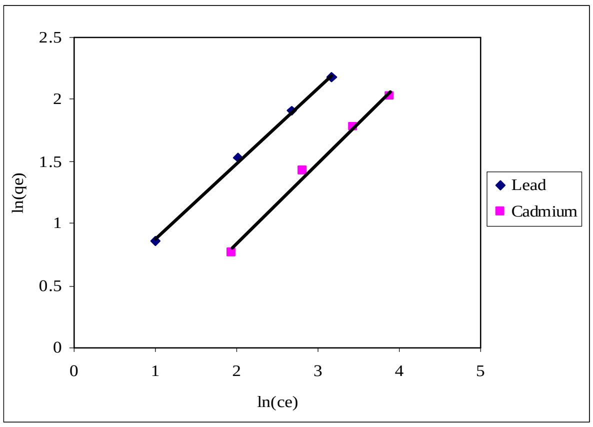

Fig. 7. Adsorption Isotherm of Pb,Cd at pH (5.5) by using Freundlich.

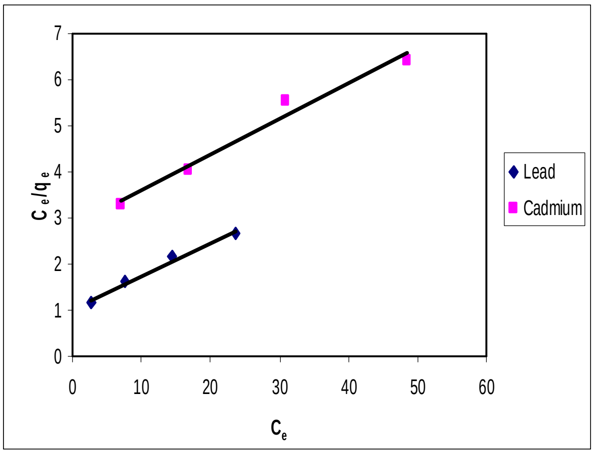

Fig. 8. Adsorption Isotherm of Pb,Cd at pH (5.5) by using Langmuir.

Table 3,
Parameter of Isotherms for Cd ,Pb and Correlation Coefficient for Freundlich and Langmuir Isotherm R^2.

Kinetic model	Parameters	Pb^{+2}	Cd^{+2}
Langmuir	q_m (mg/g)	13.9	12.85
	b L/mg	0.070	0.028
	R^2	0.9867	0.9734
Freundlich	$k_f \frac{mg}{g}(\frac{L}{mg})^{\frac{1}{n}}$	1.305	0.621
	n	1.636	1.529
	R^2	0.9983	0.9928

4. Conclusion

The investigation show that Al-Khriet a local natural agent which is are abundant and low cost, therefore can be used as a bioadsorbent for removal Pb^{+2}, Cd^{+2} ions from aqueous solutions. It was noted that removal process increased with contact time and attains saturation in about 4 h. The rapid kinetic of adsorption process has significant practical importance ensuring efficiency and economy. Also the adsorption of Pb^{+2}, Cd^{+2} on Al-Khriet was dependent on initial concentration and dosage of adsorbent. Adsorption capacity for cadmium was less than that for lead , The highest adsorption capacity was for lead (96%) and for cadmium (90%) with 50 ppm ions concentration, 1 gram dosage of adsorbent and pH 5.5, while the mixed heavy metal were reduced at about 8% for Pb and 12% for cadmium. In this study of kinetic of adsorption, the PSOM provides better correlation of sorption data than the PFOM , while the adorption equilibrium was better described by Freunlich model than Langmuir model.

Hence the material Al-Khriet under consideration would be useful economical treatment of waste water containing lead and cadmium metal.

5. References

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استخدام الخريط كماده مازه لازاله ايونات الرصاص والكادميوم من المحاليل المائيه

مها هادي مصطفى الحسني
قسم الهندسة الكيمياوية/ كلية الهندسة/ جامعة بغداد

الخلاصة

يهدف البحث الى استخدام النفايات الزراعيه المتوفره محليا وباقل كلفه لازالة المركبات الثقيله كالرصاص والكاديميوم من المحاليل المائيه كالخريط وهو ماده موجوده في سيقان نبات البردي كماده مازه. تم دراسة تأثير تركيز الماده المازه، تركيز أيونات الرصاص والكاديميوم بصوره منفرده وممزجه معا وزمن الأمتزاز عن النسبه الموئيه للأزاله والكميه الممتزه . تم الحصول عاى نسبه ازاله للرصاص ٩٦% وللكاديميوم ٩٠% عن الظروف التشغيليه ، درجه حامضيه ٥,٥ وكمية الماده المازه ١ غم وتركيز الأيونات ٥٠ ملغم لكل لتر وزمن الأمتزاز ٤ ساعه وعند مزج الأيونات قلت نسبة الأمتزاز بحوالي ٨% للرصاص و١٢% للكاديميوم بسب ظاهرة التزاحم والتنافس على المراكز الفعاله للخريط . تم استخدام معادلة لانكماير وفريندلج بشكل ناجح , وكان استخدام معادله لانكماير لتمثيل نتائج امتزاز كل من الأيونات بشكل افضل من معادله فريندلج حيث كان معدل ثابت لانكماير ١,٣٠٥ و ٠,٦٢١ ملغم\ غم لكل من الرصاص والكاديميوم على التوالي بينما حركية عملية الأمتصاص تمثلت بمعادله من الدرجه الثانيه حيث كان معدل ثابت الأمتصاص ٠,٠٦١ و٠,٠١٢٥ملغم\غم دقيقه لكل من الرصاص والكاديميوم على التوالي.