

New solid phase extractor for separation of Cadmium(II) based on agricultural waste.

Tariq S.Najim , Safana A.Farhan and Rasha M.Dadoosh*

Polymer Research Unit, College of Science, Mustansiriya University, Baghdad-Iraq

**Email: tariq_pru@yahoo.com*

Abstract

Myrtus Communis Leaves (MCL) have been investigated for their ability to remove cadmium ions from aqueous solution using batch and column techniques. It has been observed that MCL was effective biosorbent for removing of Cd(II) ions, moreover the biosorbent is cheap and biodegradable. The adsorption of Cd(II) onto MCL was found to be pH dependent and maximum removal of Cd(II) ions was obtained at pH 7. More than 97% of Cd(II) ions were removed at initial concentration of 20 mg/L and adsorbent weight of 14 g/L. The equilibrium data were fitted with the Langmuir and Freundlich isotherm models. On the other hand, the experimental data were best fitted with the Pseudo-second-order kinetic with correlation coefficient $R^2=1$. The maximum adsorption capacity estimated from Langmuir isotherm was found to be 33 mg/g at 25°C.

Introduction

The metals of the most immediate concern are cadmium, nickel copper, mercury, lead, chromium and zinc. Cadmium ion Cd(II) is one of the main heavy metal pollutants in storm water runoff, has been classified as a very toxic heavy metal.

Heavy metal may be found in wastewater discharges from the manufacture of cadmium-nikel batteries, fertilizers, pesticides, lead mining, pigments, dyes and textile operation (

Salim et al.1992; Grayson & Othumer 1978).

The major ill-effects caused by cadmium ions are inhibition of enzymes activity, headache, nausea and vomiting, chest pain, serious damage to kidneys and bones (Volesky 1990). There are many treatment processes that can be used for the removal of metal ions from aqueous and certainly the cost plays an important, if not crucial, role for determining which one is to be applied. These include chemical precipitation (Esalah et al. 2000),

biosorption (Sag et al. 2002), electrolytic recovery, membrane separation (Canet et al. 2002), activated carbon adsorption (Toles & Marshall 2002), liquid-liquid extraction (LLE) and solid phase extraction (SPE) techniques (Farajzadeh et al.2000; Soliman & Ahmed 2009; Soliman & Ahmed 2010). The SPE technique has several advantages over other techniques, including stability and reusability of the solid phase, reach of high preconcentration factors, easiness of separation, and no need for organic solvents. The application of activated carbon in water treatment is a well known and efficient technology for removal of toxic heavy metal ions. But the high cost of activated carbon inhibits its large-scale use as adsorbent. Then, the search for effective and economical adsorbent pushes the efforts of the researchers to draw their interest on cheaper materials like natural products such as agricultural wastes (Ahmed 2011; Shukla et al. 2005; Najim & Yassin 2009; Gupta & Babu 2009; Argun et al. 2007; ElNemr et al. 2007). They are available in large quantities and have a low price and a good mechanical stability. In this aspect, peppermint leaves (agricultural waste) were examined in our laboratory for its capability of Cr(VI) uptake from aqueous solution. It has a good capacity for binding metal cations due to hydroxyl, carboxylic, amino, amide and phenolic groups present in their structure (unpublished results). The main objective of this paper is to employ, simple

and direct extraction method, SPE, and low cost adsorbent, Myrtus Communis leaves (MCL) for the removal of cadmium (II) ions from aqueous solutions using both batch and column techniques.

Methods

Preparation of biosorbent

The MCL were collected from MC plants grown in Baghdad area, dried and ground with laboratory scale grinder to particle size 200-500 μ m. The leaves powder was washed several times with deionized water over six to seven days at room temperature in order to remove all soluble organic or inorganic materials.

Preparation of Cd(II) solution

Cadmium nitrate obtained from fluka of purity 99.8% was used for preparation of stock solution. Stock solution (500mg/L) of Cd(II) was prepared by dissolving an appropriate weight in deionized water and diluted to get the desired concentrations of Cd(II).

Biosorption studies

Biosorption experiments were carried out with 50 ml Cd(II) solution of desired concentration, mixing 0.1g adsorbent in a 100ml flask. The mixture was agitated at 140 rpm for 120min. The influence of hydrogen ion concentration on the biosorption process was studied over a pH range of 3.0-8.0, with adjustments being made using 0.1M Hcl or 0.1M NaOH. The effect of Cd(II) concentration was studied in the range from

10 to 200 mg L⁻¹ at pH 7.0. The effect of temperature on the biosorption capacity was investigated in the range from 25 to 55 °C at pH 7.0. The adsorbent dose effect was studied in the range 1 to 14 g/L at pH 7.0.

The biosorption capacity, q_e (mg/g), was calculated as follows (ElNemr et al. 2007):

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

The removal efficiency of Cd(II) by adsorbent, was calculated using the following equation(ElNemr et al. 2007):

$$R\% = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Where, C_o and C_e are the initial and final concentrations (mg/L) of Cd(II) ions, respectively, W is the adsorbent dosage (g) and V the volume of solution (L).

All experiments were carried out at least three times and the average values were taken into consideration. The residual cadmium ions in the filtrate were analyzed by atomic absorption spectrometer type (Phenoix-696).

FTIR spectra of virgin and loaded biosorbent were recorded by using Jasco 4200

spectrophotometer in the range of 400-4000 cm⁻¹ using KBr disk.

Results and discussion

Characterization of the adsorbent

FTIR spectra for both fresh and Cd(II) loaded MCL were presented in Fig.1. A peak at 3500-3200 cm⁻¹ is due to stretching vibrations of the surface hydroxyl group and N-H bond of amino groups. The absorption peak at 2925 cm⁻¹ could be assigned to -CH stretching vibration of -CH₃ and -CH₂ functional groups. The distinct peak observed in 1733 cm⁻¹ and 1653 cm⁻¹ characterize carbonyl groups stretching from aldehydes is characteristic peak of polysaccharides (Sheng et al. 2004; Srividya & Mohanty 2009). The minor shift of the peak from 1027 to 1025 cm⁻¹ and carbonyl group from 1733 to 1730cm⁻¹ Suggest the involvement of C-O group in binding of Cd(II). The functional groups that are responsible for a sorption of metal ions are hydroxyl, carboxyl, carbonyl, amine, amide, sulfonate, and imidazole (Pradhan et al. 2007; Volesky 2007).

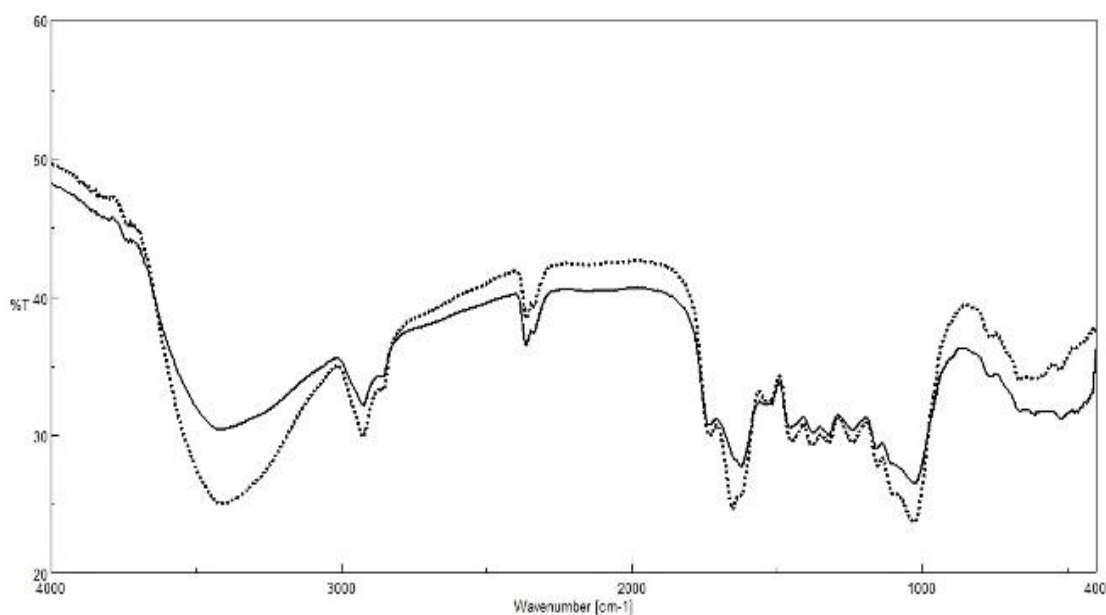


Figure (1) FTIR of MCL (dotted line) and Cd(II) loaded MCL (solid line).

Effect of pH on Cd (II) on binding of MCL

The effect of pH on the adsorption of Cd(II) by MCL is presented in Fig.2. The pH of the aqueous solution is an important parameter that controlled the adsorption process. Adsorption capacity of adsorbent increased remarkably with increasing pH values up to 7, and then increase rate was slower until pH 8 due to precipitation of Cd ions at higher pH values. This is clear as shown in Fig.2, for the

uptake of Cd(II) ions as a function of pH (3.0-8.0). pH 7.0 was taken as the maximum binding capacity, although, the binding capacity at pH 8.0 is higher than pH 7.0, due to the presence of cadmium hydroxide at pH higher than 8 (Gaballah & Kilbertus 1998). The equilibrium concentration C_e is decreased as the pH of solution is increase, Fig.2, due to the increase in binding of Cd(II) by the MCL.

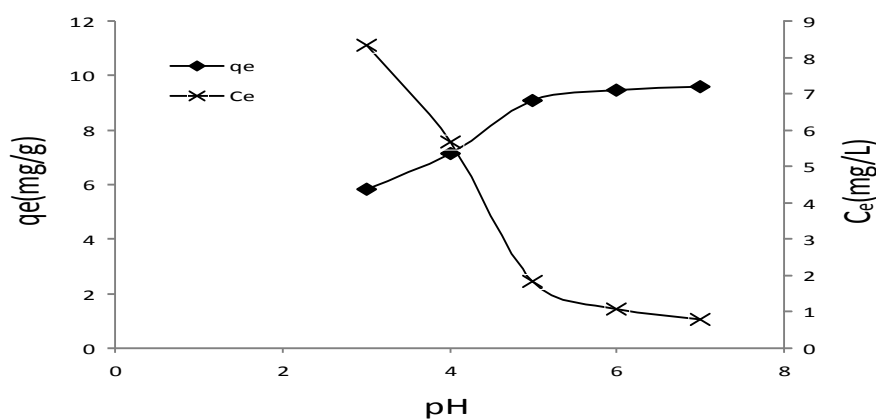


Figure (2) Effect of pH on adsorption of Cd(II) onto MCL.

Effect of MCL weight

The weight of MCL adsorbent was varied from 1 to 14 g/L keeping all the other experimental variables, viz., pH 7.0, initial Cd(II) concentration 20 mg/L, and contact

time 80 min. constant. Fig.3 presents the adsorbent weight versus adsorption capacity q_e and removal efficiency R%. It may be observed that on increasing the adsorbent

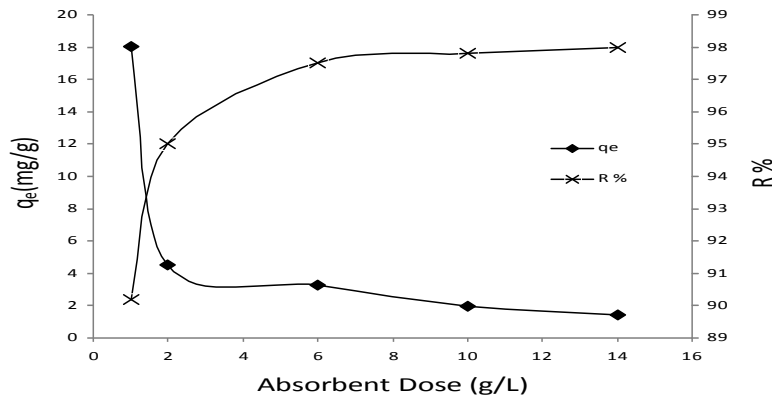


Figure (3) Effect of adsorbent dose on the adsorption of Cd(II) onto MCL.

weight the removal efficiency increased up to concentration of 8 g/ L then remained almost constant, while the adsorption capacity decreased with increasing weight of MCL.

Effect of contact time

Contact time is an important factor in the process of evaluation of the MCL, the batch experiments were performed at different contact times with a fixed sorbent concentration 1.0 g/L, Cd(II) concentration 20 mg/L at pH 7.0 and 50 ml reaction solution, these experiments were done at different temperature 25, 35, 45 and 55°C, results of adsorption capacity of Cd(II) as a function of contact time is presented in Fig.4. the equilibrium is reached within the first 50 min of contact time.

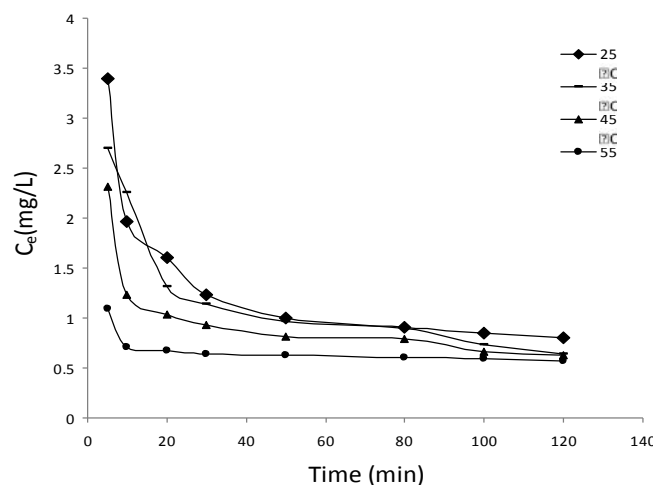


Figure (4) Effect of contact time on the adsorption of Cd(II) onto MCL.

Kinetic studies

In order to define the adsorption kinetics of heavy metal ions, kinetic parameters for the adsorption process were studied for contact times ranging between 5 to 120 min monitoring the adsorption capacity of the adsorbent by the Cd(II) ions. For affixed concentration of Cd(II) and fixed adsorbent mass, the retention of Cd(II) ions increased with increasing contact time. The experimental data were regressed against the pseudo-first order model represented by the following linear equation (Ho & McKay 1999):

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (3)$$

and pseudo-second-order kinetic model (Ozturk & Kavak 2005):

$$t/q_t = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad (4)$$

Where q_e and q_t are the adsorption capacity at equilibrium and at time t respectively, k_1 , k_2 are the rate constants of the pseudo-first-order and pseudo-second-order kinetics. The \log

$(q_e - q_t)$ was plotted against time (t) of the first-order kinetic model (plot is not shown), and t/q_t versus (t) of the second-order kinetic Fig.5. The slopes and intercepts of these curves were used to determine the pseudo-first-order and pseudo-second-order constants k_1 and k_2 and the equilibrium capacity q_e . The calculated (cal) values q_{cal} from the pseudo-first-order kinetics model was dramatically lower than the experimental (exp) values q_{exp} Table1. However, the pseudo-second-order kinetics model (Fig.4, Table1) provided a near-perfect match between the theoretical and experimental q_e values and the correlation coefficient values $R^2 = 1$ (table 1). As a result, the sorption system appears to follow pseudo-second-order reaction kinetic. The pseudo-second-order rate constants for Cd(II) adsorption on MC were 0.124, 0.123, 0.223 and 1.02 at 25, 35, 45 and 55°C respectively and q_e (cal) values were 9.65, 9.69, 9.69 and 9.71 at 25, 35, 45 and 55°C respectively. From these results it is obvious that the adsorption of Cd(II) onto MCL is enhanced by temperature elevation, which is an evidence for the endothermic process.

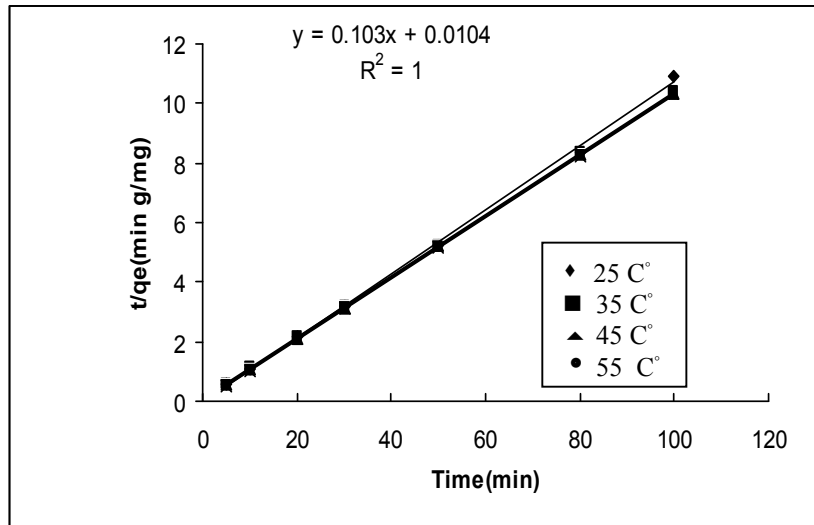


Figure (5) Pseudo-second order plot of the adsorption of Cd(II) onto MCL at different temperatures

Table (1) The pseudo-first-order and pseudo-second-order constants of the adsorption of Cd(II) onto MC at different temperatures.

Temp (°C)	Q _e exp (mg /g)	Pseudo-first-order Kinetics			Pseudo-second-order kinetics		
		Q _e cal (mg/g)	k ₁ (min ⁻¹)	R ²	Q _e cal (mg/g)	k ₂ (g mg ⁻¹ min ⁻¹)	R ²
25	9.60	0.951	0.0394	0.9598	9.65	0.124	1.00
35	9.68	0.877	0.0290	0.8971	9.69	0.123	1.00
45	9.69	0.516	0.0300	0.8688	9.69	0.223	1.00
55	9.71	0.140	0.0300	0.7723	9.71	1.020	1.00

Determination of adsorption isotherms

Adsorption isotherms or capacity studies are of fundamental importance in the design of adsorption systems since they indicate how the metal ions are partitioned between the

adsorbent and liquid phases at equilibrium as a function of increasing metal concentration. When an adsorbent and metal ion solution is placed in contact, the concentration of metal ions on the adsorbent will increase until a

dynamic equilibrium is reached, at this point; there is a defined distribution of metal ions between the solid and liquid phases. Therefore, the Cd(II) adsorption capacities at pH 7 were calculated by means of least squares regression of the linear isotherm equation. The obtained experimental data were applied to the Langmuir adsorption isotherm(Langmuir 1918) and linear expression of this model has been demonstrated as:

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_{\max} \times b}\right) + \left(\frac{1}{Q_{\max}}\right)C_e \quad (5)$$

Where q_e is the Cd(II) ions uptake per unit weight of MCL (mg/g); C_e (mg/L) is the Cd(II) concentration in solution; Q_m (mg/g) and $b(\text{Lmg}^{-1})$ are the Langmuir constants related to the theoretical sorption capacity and energy of adsorption, respectively.

According to equation 5, C_e/q_e was plotted versus C_e , from the intercept and slope of Fig.6, the constant b and Q_m were determined and tabulated in table 2. The essential characteristics of Langmuir isotherm can be expressed in term of dimensionless

equilibrium parameter R_L (Weber & Chakravorti 1974), which is defined as follows:

$$R_L = \frac{1}{1 + b \times c_o}$$

The value of R_L indicates the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The R_L for Cd(II) sorption supports a highly favorable process based on Langmuir model table 2.

The liner form of Freundlich isotherm model can be expressed as follows(Freundlich 1907);

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

Where, K_F and $1/n$ are Freundlich constants (indicators of the sorption capacity and intensity, respectively). The K_F and $1/n$ can be calculated from the intercept and slope of equation 6 respectively, the values are presented in Table 2, Fig.7. It is clear from correlation coefficients of Langmuir and Freundlich equations that the data fitting well with both models.

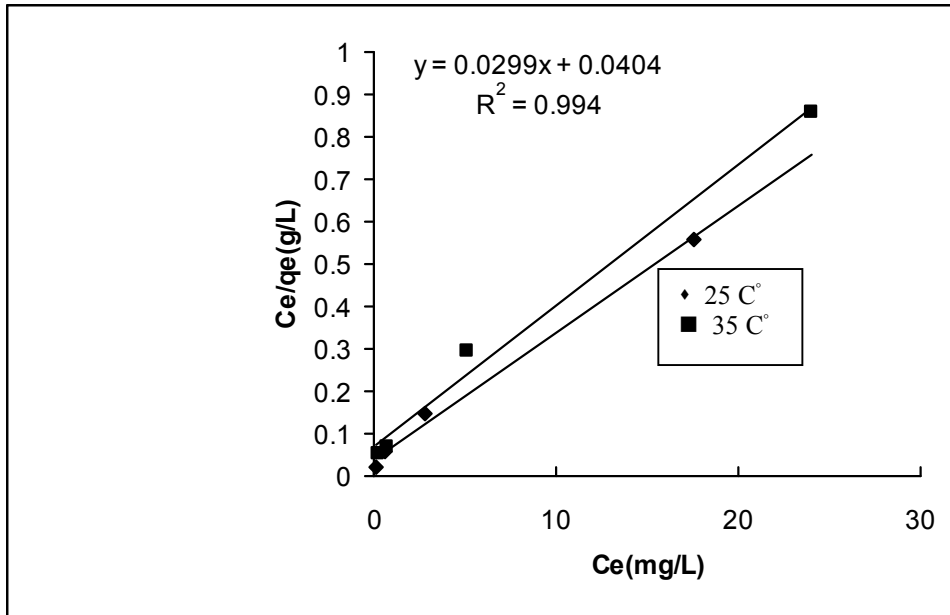


Figure (6) Langmuir plot of the adsorption of Cd(II) onto MCL .

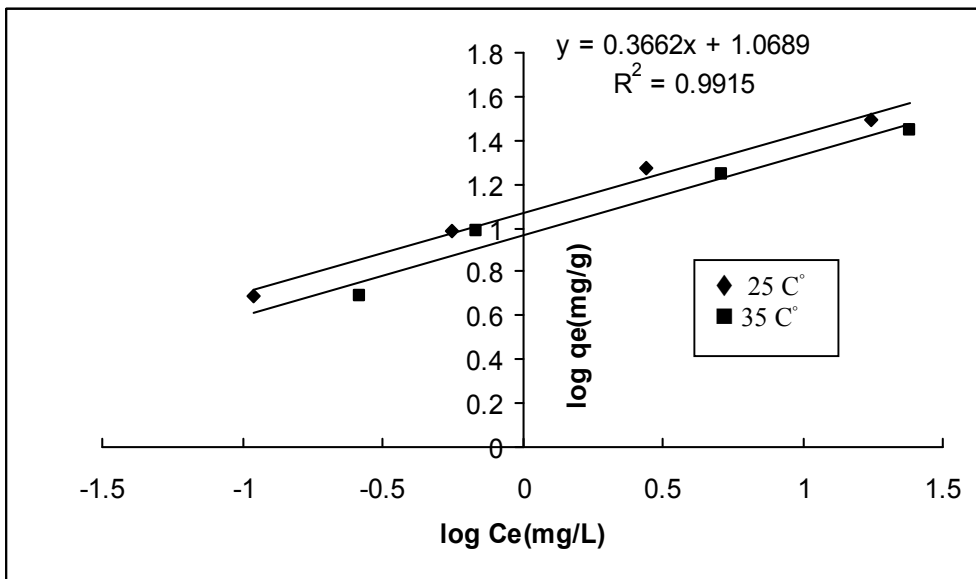


Figure (7) Freundlich plot of Cd(II) adsorption onto MCL at 25 and 35°C.

Table (2) The Langmuir and Freundlich parameters and correlation coefficients of the adsorption of Cd(II) onto MCL at 25 and 35° C.

Temperature (K)	Langmuir isotherm			Freundlich isotherm			
	$Q_{\max}(\text{mg/g})$	b	R^2	R_L	n	K_f	R^2
298	33.4	0.74	0.994	0.06	2.73	11.72	0.9915
308	30.0	0.48	0.9903	0.09	2.73	9.27	0.9653

Column studies

A glass column of 40cm length and 2cm internal diameter was used. Different bed height of MCL were put between two layers of glass wool. Then 50 ml of Cd(II) solution of 20 mg/L after adjusted at pH7 was passed through the column with flow rate of 1.5

ml/min. Plot of C_e/C_0 versus time was shown in Fig.8.

The quantitative recovery values of Cd(II) as shown in Fig.3 and Fig.8 indicate the suitability of MCL for selective removal of Cd(II) from polluted water samples either by batch or column techniques.

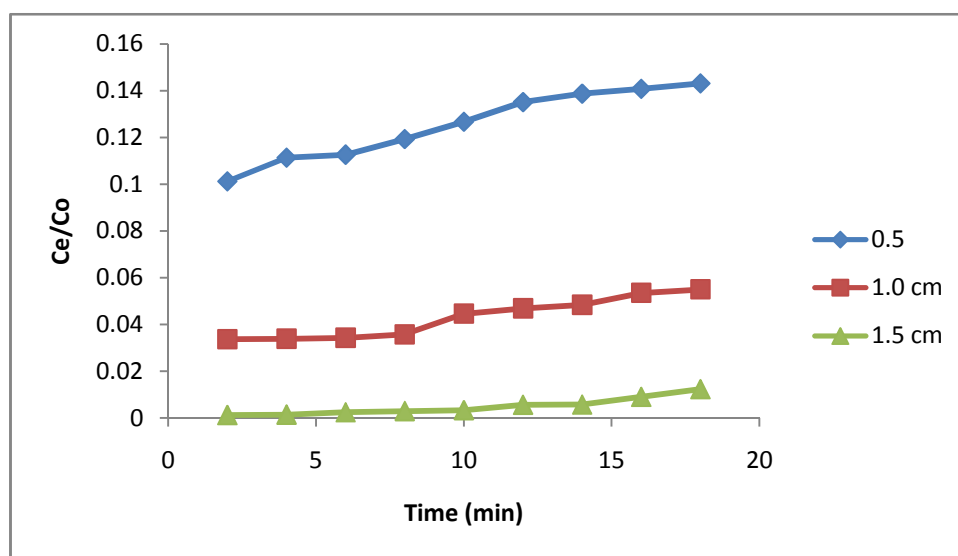


Figure 8. Effect of bed height on uptake of Cd(II) at flow rate 1.5 ml/min.

Conclusion

It was found that MCL is efficient for removal of Cd(II) from aqueous solution due to the presence of effective functional groups in its structure, it removes more than 97% of Cd(II) ions at pH7, when, the Cd(II)

concentration was 20 mg/L and the adsorbent weight 14 g/L. Pseudo-second-order equation was fitted very well to the experimental data with correlation coefficient $R^2=1$. Moreover, the MCL is environment friendly.

Acknowledgement

The authors are gratefully acknowledge the financial support of this work by the Arab Science and Technology Foundation (Project Number140-10).

References

- Ahmed, S.A.(2011). Batch and fixed- bed column techniques for removal of Cu(II) and Fe(II) using Carbohydrate natural polymer modified complexing agent. *Carbohydrates Polymers*, 83, 1470-1478.
- Argun,M.E., Dursun, S., Ozdemir, C., and Karatas,M. (2007). Heavy metal adsorption by modified oak sawdust: Thermodynamic and kinetics. *Journal of Hazardous Materials* 141,77-85.
- Canet, L., Ilpide, M.,& Seta, P.(2002). Efficient facilitated transport of lead, cadmium, zinc and silver across a flat sheet–supported liquid membrane mediated by lasalocid A. *Separation Science and Technology*, 37,1851-1860.
- ElNemr, A., Elsikaily, A., khaled, A., and Abdelwahab, O. (2007). Removal of toxic Cr(VI) from aqueous solution by activated carbon using *Casuarinas equisetifolia*. *Chemistry and Ecology*, 23,(2),119-129.
- Esalah, J.O., Weber M.E., & Vera, J.H.(2000). Removal of Lead, Cadmium, and Zinc from aqueous solutions by precipitation with sodium di-(n-octyl) phosphinate. *The Canadian Journal of Chemical Engineering*, 78, 948-954.
- Farajzadeh, M.A., Bahram,M., Zorita, S., & Vera, J.H.(2000). Optimization and application of homogeneous liquid –liquid extraction in preconcentration of copper(II) in a ternary solvent system. *J.Hazardous Materials*, 161,1535-1543.
- Freundlich, H. (1907). Ueber die adsorption in loesungen. *J.Physical Chemistry*, 7, 385-470.
- Gaballah, I., Kilbertus, G. (1998). Recovery of heavy metal ions through decontamination of synthetic solutions and industrial effluents using modified barks. *J. Geochem.Explor.*, 62, 241-286.
- Grayson, M., and Othumer, K.(1978). *Encyclopedia of Chemical Technology* 43rd edn., John Wiley and Sons.
- Gupta, S., and Babu, B.V. (2009). Removal of toxic Cr(VI) from aqueous solutions using sawdust as adsorbent: equilibrium,kinetic and regeneration studies. *Chemical Engineering Journal*,150, 352-365.
- Ho, Y.S., and Mckay, G. (1999). Comparative sorption kinetic studies of dyes and aromatic compounds onto flyash. *J. Environ. Sci. and Health A34*, 1179-1204.
- Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, Mica and platinum. *J. American Chemical Society* 40, 1361-1403.
- Najim,T.S., and Yassin,S.A.(2009). Removal of Cr(VI) from aqueous solutions using modified pomegranate Peel: equilibrium

- and kinetic studies. *E-Journal of Chemistry* 6(S1), S129-S142.
- Ozturk, N., and Kavak, D. (2005). Adsorption of boron from aqueous solution using flyash: batch and column studies. *J.Hazardous Materials*, B127, 81-88.
- Pradhan, S., Singh, S. and Rai, L.C.(2007). Characterization of various functional groups present in the capsule of *Microcystis* and study of their role in biosorption of Fe, Ni, Cr, *Bioresour. Technol.*, 98, 595-601.
- Sag, Y., Akcael, B., & Kutsal, T.(2002). Ternary biosorption equilibria of Chromium(VI), Copper(II) and Cadmium(II) on *Rhizopus Arrhizus*. *Separation Science and Technology*, 37, 279-309.
- Salim, R., Al-Subu, M.M, and Sahrhage, E. (1992). Uptake of cadmium from water by beech leaves *J. Environ. Sci. Health*, A27 (3), 603- 627.
- Sheng, P.X., Ting, Y.P., Chen, J.P., and Hong, L. (2004). Sorption of lead, copper, cadmium, zinc and nikel by marine algae biomass: characterization of biosorptive capacity and investigation of mechanism. *J.Colloid Interface Sci.*, 275, 131-141.
- Shukla, S.S., Yu, L.J., Dorris, K.L.,& Shukla,A. (2005). Removal of Nikel from aqueous solutions by sawdust. *Journal of Hazardous Materials*, B121, 243-246.
- Soliman, E.M., & Ahmed , S.A.(2010) Solid-phase extractor based on 8-aminoquiniline and 2-aminopyridine covalently bonded to silica gel for the selective separation and determination of calcium in natural water and pharmaceutical samples. *Analytical Sciences*, 26, 473-478.
- Soliman, E.M., & Ahmed, S.A.(2009). Selective separation of silver(I), Mercury(II) ions in natural water samples using alumina modified thiouracil derivatives as new solid phase extractors. *International Journal of Environmental Chemistry*, 89,389-406.
- Srividya, K., and Mohanty, K. (2009). Biosorption of hexavalent chromium from aqueous by *Catla catla* scales: Equilibrium and kinetic studies. *Chem. Eng. J.* 155, 666-673.
- Toles, C.A., & Marshall W.E.(2002). Copper ion removal by almond shell carbons and commercial carbons: Batch and column studies, *Separation Science & Technology*, 37, 2369-2383.
- Volesky, B. (2007). *Water Res.*, 41, 4017-4029.
- Volesky, B.(1990). *Biosorption of heavy metals*. CRC Press, Boca Raton, FL.
- Weber, T.W., and Chakravorti, R.K.(1974). Pore and solid diffusion models for fixed-bed adsorber. *AIChE Journal*, 20,228.

وسط صلب جديد لفصل الكاديوم الثنائي يعتمد على النفايات الزراعية

طارق سهيل نجم ، سفانه احمد فرحان و رشا منعم دعدوش

وحدة ابحاث البوليمرات والتطبيقات الصناعية- كلية العلوم- الجامعة المستنصرية - بغداد - العراق

المخلص

تم استخدام اوراق نبات الياس لدراسة قابليتها على ازالة ايونات الكاديوم من الاوساط المائيه باستخدام التقنيه المتقطعه وتقنية العمود. وجدنا بان اوراق الياس كفوءه كماده مازة في ازالة ايونات الكاديوم اضافيه الى ان هذه الماده رخيصة الثمن وقابله للتحلل البيولوجي. وجدنا ايضا بان عملية امتزاز ايونات الكاديوم على اوراق نبات الياس تعتمد على الداله الحامضيه وان اعلى نسبة امتزاز تحصل في pH 7 ، وان اكثر من 97% من ايونات الكاديوم تمت ازلتها عند تركيز الكاديوم الابتدائي 20 mg/L عندما يكون وزن الماده المازة 14mg/L . تم تطبيق نتائج الامتزاز على ايزوثيرمات لانكماير و فريندلش ، وجدنا ان نتائج الامتزاز تنطبق تماما على الحركيه من الدرجه الثانيه الكاذبه مع سعة امتزاز قصوى والتي تم حسابها من ايزوثيرم لانكماير ووجدت بحدود 33 mg/g بدرجه 25°C .