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Removal of Pb(II), Cr(VI) and Zn(II) ions from water by adsorption onto marine fouling

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Abstract

Marine fouling (shell fragment tube worm, (*Mercierella Enigmatica*) was used as adsorbent for the removal of Cr^{6+}, Zn^{2+} and Pb^{2+} from mono - and multi-metal ion aqueous solutions through batch adsorption process . Removal efficiency from synthetic aqueous solutions and real wastewater was investigated under various conditions such as variable concentration of metal ion, amount of adsorbent, pH and contact time. Equilibrium data were analyzed by the Langmuir and Freundlich isotherm model. Langmuir isotherm fits the data better in both single and multi-component systems. The kinetic data were found to follow the pseudo-second-order reaction model. The study also showed that shell can be efficiently used as low cost material for removal of metal ions.

Keywords: marine fouling, heavy metals, adsorption, kinetic, wastewater.

1. Introduction

Adsorption is a surface process that occurs when a solute is selectively retained on the surface of an adsorbent forming a thin layer of the adsorbate (Doina et al. 2009). Thus adsorption finds its use in the removal of dissolved substances from water with careful choice of adsorbent and adsorbate (Oladoja et al. 2008). It involves selective retention of the adsorbate to the adsorption sites of the adsorbent (Yahya et al. 2007). Heavy metals pollution is currently of great concern due to its increased awareness of the potentially hazardous effects of elevated levels of these materials in the environment (Fu and Wang 2011). According to the list of priority pollutants of the US Environmental Protection Agency (EPA), arsenic, chromium, cobalt, nickel, copper, zinc, silver, cadmium, mercury, thallium, titanium, selenium and lead have become a public health concern because they are non-biodegradable and tend to accumulate in living organisms causing several diseases that affect the kidney, nervous, hematopoietic and gastrointestinal systems of humans (Argun and Dursum 2008). As a result of the degree of the problems caused by heavy metals pollution, removal of heavy metals from wastewater is important (Chand et al. 1994). Heavy metals removal from aqueous solutions has been a focus area of research in recent years. Many technologies have been developed for removing HMs including chemical precipitation, ion exchange, ultrafiltration,reverse osmosis, electrodialysis, and adsorption (Barakat 2011). Of all the various water-treatment processes, adsorption is generally preferred since it is considered as one of the most effective and economical techniques used to remove heavy metals from water (Bhattacharya et al. 2006; Ijagbemi et al. 2009).

Recently efforts have been made to use cheap and available adsorbents such as coconut shell, orange peel, rice husk, peanut husk and sawdust as adsorbents(Iqbal Ahmad 2005) to remove heavy metals from wastewater(Vaishnav etl. 2012) .

This work oriented to use marine fouling (shell fragment tube worm (*Mercierella Enigmatica*) as adsorbent to remove Cr^{6+}, Zn^{2+} and Pb^{2+} present in leather tanning wastewater. Parameters such as pH, variable concentration of metal ions , adsorbent dosage and contact time, were investigated at 25°C While the pseudo first-order and pseudo second-order models were used to analyze the kinetic data and the Langmuir and Freundlich isotherm models were used to analyze equilibrium data .

2. Material and Methods

2.1 Adsorbent Preparation:

Marine fouling (shell fragment tube worm, (*Mercierella Enigmatica*) was obtained from The Eastern Harbour of Alexandria. It was washed several times with hydrogen peroxide (H_2O_2) and distilled water to eradicate possible strange materials present in it until the pH of washed water range between 6 and 7. Washed sample material was dried in an oven at 70°C for a period of 24h and then crushed with crusher to reduce the size.

Table.1. XRD and FTIR data of marine fouling

(XRD)Chemical composition			
Formula	**(wt %)**	**FTIR data(function group)**	
Ca	12.89%	(–C–X)	716
Si	3.78%	(–C–X)	863
C	27.45%	(–C–H)	1418
SiC	5.14%	C=C	1638
$CaSi_2$	2.95%	(–C–H)	2924
CaC_2	7.66%	(–O–H)	34414

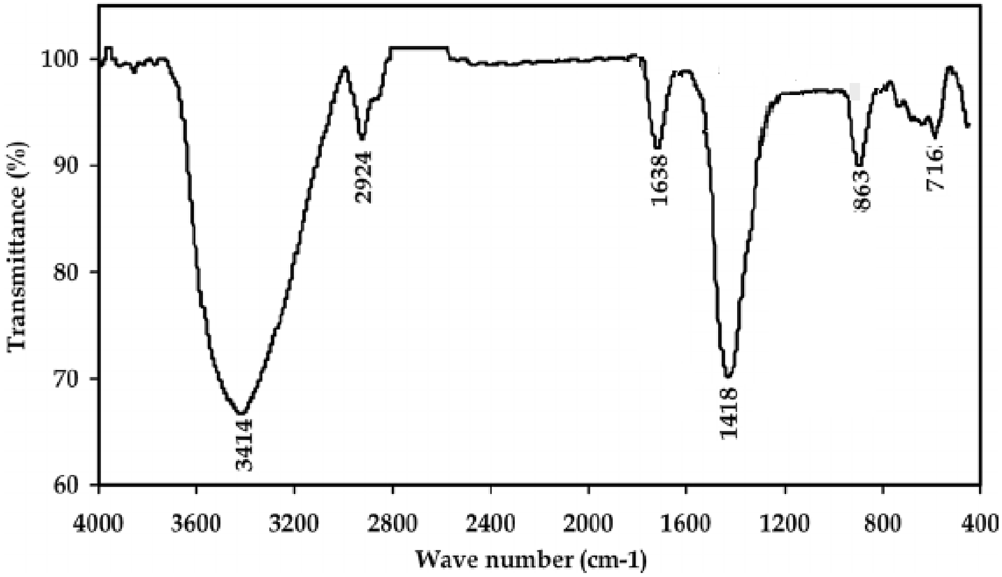

Fig. 1. FTIR spectrum of marine fouling

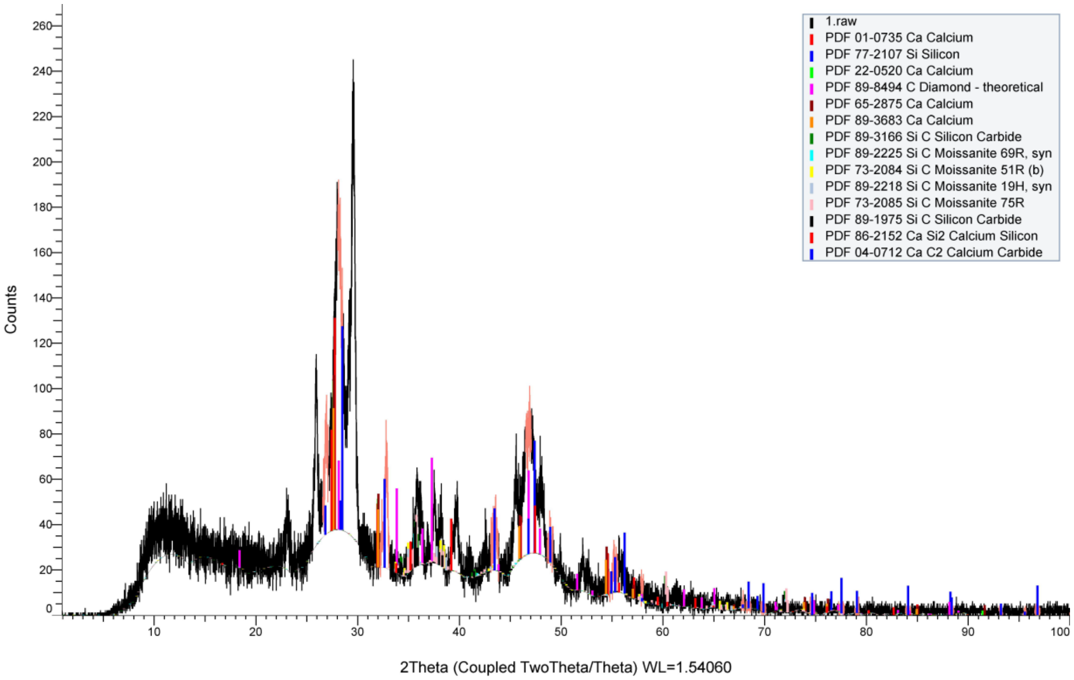

Fig. 2. XRD of marine fouling

2.2 Metal analysis reagents:

Stock solutions of Cr^{+6}, Zn^{+2} and Pb^{+2} (1,000 mg L^{-1}) were prepared by dissolving an appropriate amount of analytical grade reagents lead nitrate $Pb(NO_3)_2$ [Drug houses (India), Graham Road, Bombay-1], zinc acetate $Zn(O_2CCH_3)_2$ (Glaxo Laboratories India,Bombay) and potassium dichromate $K_2Cr_2O_7$ (Ranbaxy Laboratories, India) in double distilled water (DDW). pH Buffer solutions (pH 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0) were prepared from 1.0 M hydrochloric acid solution HCL and 1.0 M sodium acetate anhydrous solution CH_3COONa by mixing the appropriate volumes of the two solutions and diluting to 1.0 L. The pH-value of resulting solutions was adjusted by a pH meter, WTW-inolab, Germany. The metal concentration in aqueous solutions was determined by flame atomic absorption spectrophotometer (FAAS) (Perkin Elmer 503) using a calibration curve prepared with standard metal solutions.

2.3 Batch adsorption Study:

Batch adsorption experiments were carried out by adding known amount of adsorbent to 50 ml of metal aqueous solution into a conical flask. The conical flask containing the adsorbent and metal aqueous solution was placed on a rotary shaker and shook at 300rpm at room temperature (25 °C). After the specified time, suspensions were filtered use 0.45 µm membrane filter paper. Atomic adsorption spectrophotometer was used to analyze the concentrations of the different metal ion present in the filtrate (Chowdhury et al. 2010).

In order to investigate kinetics, suspensions consisting of 1 g of adsorbent and 50 ml of 5 mg/l of metal aqueous solutions were shook from 5 to 120 min.

For the adsorption isotherm studies, 1g of adsorbent was shook with metal aqueous solutions of different concentrations (5, 10, 15, 20,25,30,35 and 40 mg/l) until equilibrium was attained. On the basis of kinetic study, 120 min time was taken as the time enough to reach the equilibrium state.

To examine the influence of solution pH on the mechanism and the capacity of the adsorption, 1 g of adsorbent was shook for 120 min with 50 ml of 5 mg/l of metal aqueous solutions at pH values ranging from1 to 8.

For studying the effect of adsorbent dosage on adsorption, 50 ml of 5 mg/l of metal aqueous solutions were shook for 120 min with different amounts of adsorbent (0.2, 0.4, 0.8 and 1g).

To see the effect of the presence of some metals together present in the industrial effluents a multi-metal system (Pb^{+2} +Cr^{+6} +Zn^{+2}) was also studied. Adsorption studies were carried out for multi-component system with same conditions as in single-component system (50 mL aqueous solution with 1 g of adsorbent agitated for 2h at room temperature). Initial metal concentration of each metal ion in multi-metal system was in the ratio of 1:1:1:1.

In all the cases, the amount of metal ions adsorbed by the adsorbent was calculated using equation :

$$q_t = (C_o - C_t)V/W$$

the mass adsorption capacity, q_e (mg/g), was calculated by:

$$q_e = (C_o - C_e)V/W$$

Where $\mathbf{C_0}$ is the initial concentration of the heavy metals in liquid phase, V is the aqueous solution volume (L). While **W** represents the adsorbent mass (g) and **C** is the residual concentrations of heavy metals in liquid phase (mg/L) at equilibrium or any time t, which defines $\mathbf{C_e}$ or $\mathbf{C_t}$ respectively.

The percentage of metal ions removed was obtained from equation:

$$R\ \% = (Co - C_t / C_o) * 100$$

2.4 Industrial wastewaters:

The wastewater sample used was collected from leather tanning factory located in The Industrial Area , Qusna ,El Menoufia, Egypt. It was carefully bottled in i 1 L polyethylene bottles that had been pre-cleaned with acid solution (1:1 HNO_3) overnight and then rinsed with deionized water. The bottles were immediately taken to the laboratory for analysis. Wastewaters were passed through a 0.45 lm membrane filter. The heavy metals present in the wastewater sample, were analyzed using the atomic-absorption spectrophotometer to determind the concentrations of $Cr^{6+,}$ Zn^{2+} and Pb^{2+}. The initial concentrations of the metal ions present in the waste water are 7.68ppm , 5.10ppm , 5.01ppm for $Cr^{6+,}$ Zn^{2+} and Pb^{+2} ,respectively .

In the experiment, 1 g of shell was added to 50 mL of wastewater and shook at 300rpm at room temperature (25 °C) for 120 min at pH 4.suspensions were filtered use 0.45 µm membrane filter paper and kept for metal analyses.

3. Results and Discussion

3.1 Effect of pH on Adsorption of Heavy Metals:

The effect of the solution pH on the adsorption of $Cr^{6+,}$ Zn^{2+} and Pb^{2+} ions onto marine fouling was investigated by changing initial solution pH values in the range of 2–8 and the results are presented in Fig. 3. As it was seen, the metal ions adsorption was highly pH-dependent. The percentage removal of metal ions (Zn^{2+} and Pb^{2+}) increased up to the pH 6. At pH 6, maximum removal the two metal ions were obtained, with 100% removal of Pb^{+2}, and 84% removal of Zn^{+2}. While maximum removal of Cr^{6+} ion was achieved at pH 2 with 96% percentage removal . The increase in percentage removal of the metal ions may be explained by the fact that at lower pH the H^+ ions and metal cations compete for the negative adsorption sites on the adsorbent surface. The number of H^+ ions exceeds that of the metal ions several times and the surface of adsorbent is most likely covered with H^+ ions, which account for less adsorption. At higher pH the adsorbent surface is deprotonated and negatively charge, making the sites available to the metal ions, which increasingly bind to adsorbent shell surface through a mechanism similar to that of exchange interactions (Gupta and Bhattacharyya 2008). Similar results were observed for the adsorption of heavy metal ions using different clay samples (Bourliva et al.2013; Jiang et al. 2010; Kumric´ et al. 2013).

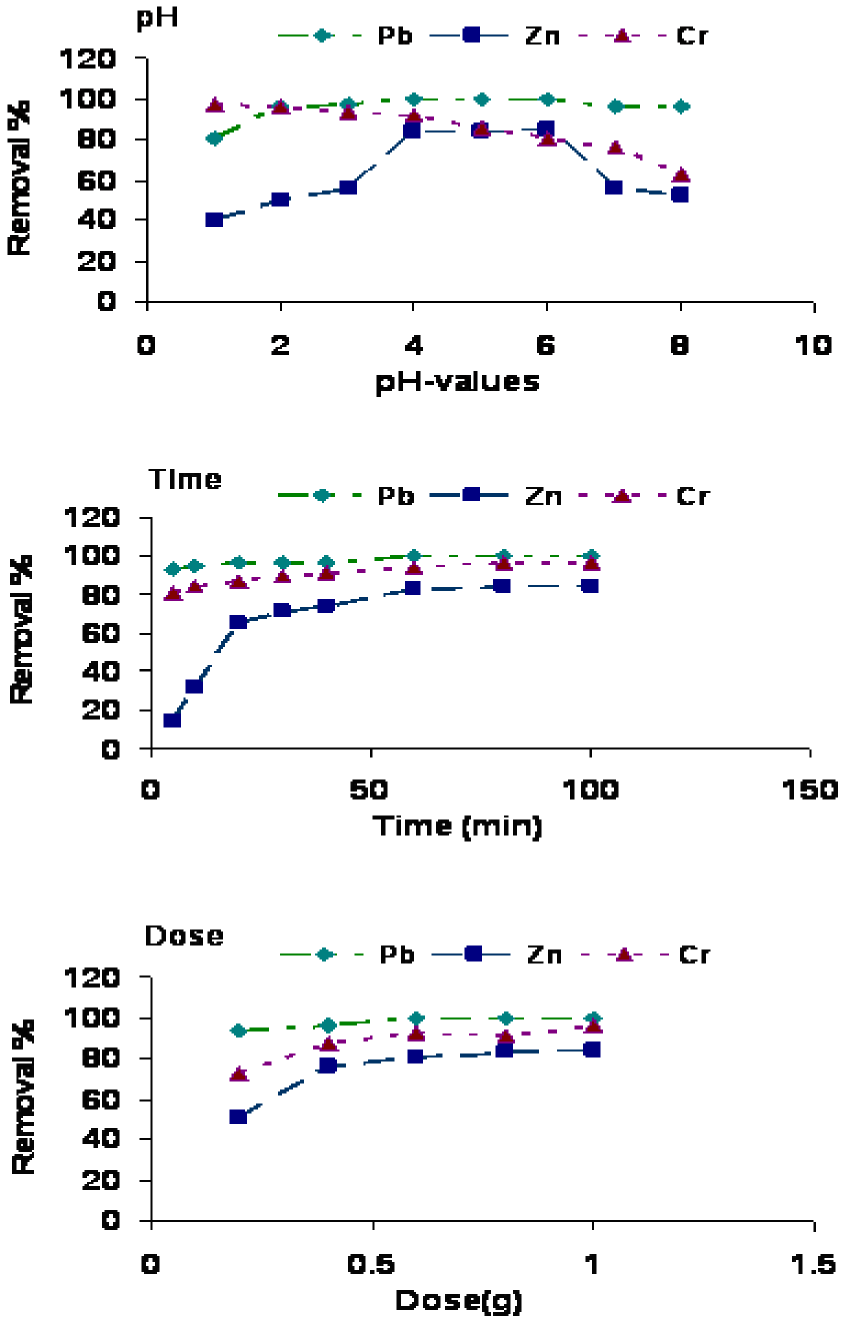

Fig. 3. Effect of pH on metal ions removal. Initial Concentration of metal ions: 5 ppm; volume of solution: 50 ml; pH range: 2– 8; adsorbent dosage 1.0 g; contact time 2h.

3.2 Effect of Contact Time on Adsorption of Heavy Metals:

The effect of contact time on the adsorption of $Cr^{6+,}$ $Zn2^{+}$ and Pb^{2+} ions was investigated at different time intervals in the range of 5-120 min and the results are presented in Fig. 3. As shown, the adsorption rate was found to be very rapid during the first 20 min of adsorption, and 96 % of Pb^{2+} , 64 % of Zn^{2+} , and 86 % of Cr^{6+} were adsorbed during this period of time. The finding is in agreement with earlier studies where fast metal ions adsorption (10–20 min) has been reported (Bourliva et al. 2013; Vieira et al. 2010). The percentage metal ions removal approached equilibrium within 40 min for Pb^{+2} , 80 min for both Cr^{+6} and 60min for Zn^{+2};with 100% removal of Pb^{+2} , 96% of Cr^{+6} and84% of Zn^{+2} . However, to ensure maximum metal removal, a 120 min contact time was applied in all experiments conducted. The increase in percentage removal of the metal ions by increasing of contact time may be explained by the fact that during the initial stage of sorption, a large number of vacant surface sites are available for adsorption. After lapse of some time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules adsorbed on the solid surface and the bulk phase (Srivastava et al. 2008).

3.3 Effect of adsorbent dosage on Adsorption of Heavy Metals:

The effect of the adsorbent dosage was studied at different shell amounts ranging from 0.2 to 1 g and the results are shown in Fig. 3. As it was found, increasing the adsorbent dosage, the adsorbed metal ions (i.e. their removal efficiencies) increased. This could be explained by the fact that an increase in the adsorbent concentration increases the surface area of the adsorbent, which increases the number of binding sites for the same liquid volume and thus the total amount of metal ions removed increases (Sen and Gomez 2011).

3.4 Adsorption Kinetics:

A kinetic study of adsorption is necessary as it provides the information about the adsorption mechanism. Two kinetic models were applied in order to establish which of them shows the best fit with experimentally obtained data (The pseudo-first-order and pseudo-second- order model). The pseudo-first-order kinetic model is expressed by the following equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Where k_1 (g/mg min) is the rate constant of pseudo-first-order adsorption, which is obtained from the slopes of the linear plots of $\ln(q_e - q_t)$ versus t (Fig.4).

The pseudo-second-order kinetic model may be expressed by the equation:

$$t/q_t = (1/k_2 q_e^2) + (t/q_e)$$

Where k_2 (g/mg min) is the equilibrium rate constant for the pseudo-second-order adsorption and can be obtained from the plot of t/qt against t (Fig. 5).

All kinetic data for the adsorption of Cr^{6+}, Zn^{2+} and Pb^{2+} ions onto adsorbent ,calculated from the related plots, are summarized in Table 2. The validity of the exploited models is verified by the correlation coefficient, r^2. Comparison of the r^2 values for two models suggests that the pseudo-second-order kinetic model fits best since its highest value. Pseudo-second-order kinetic model implies that the predominant process here is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent. Chemisorption is usually restricted to just one layer of molecules on the surface, although it may be followed by additional layers of physically adsorbed molecules (El Qada et al. 2006).

Table 2. Kinetic model parameters for adsorption of Pb^{+2}, Zn^{+2} and Cr^{+6}

Metal ions	Pseudo-first-order			Pseudo-second-order		
	k_1 (g/mg min)	q_e (mg/g)	R^2	k_1(g/mg min)	q_e (mg/g)	R^2
Pb^{+2}	0.0214	0.0165	0.8822	4.702	0.24546	0.9999
Zn^{+2}	0.0652	0.24036	0.969	0.2148	0.2525	0.9764
Cr^{+6}	0.0248	0.0439	0.9941	1.757	0.2464	0.9996

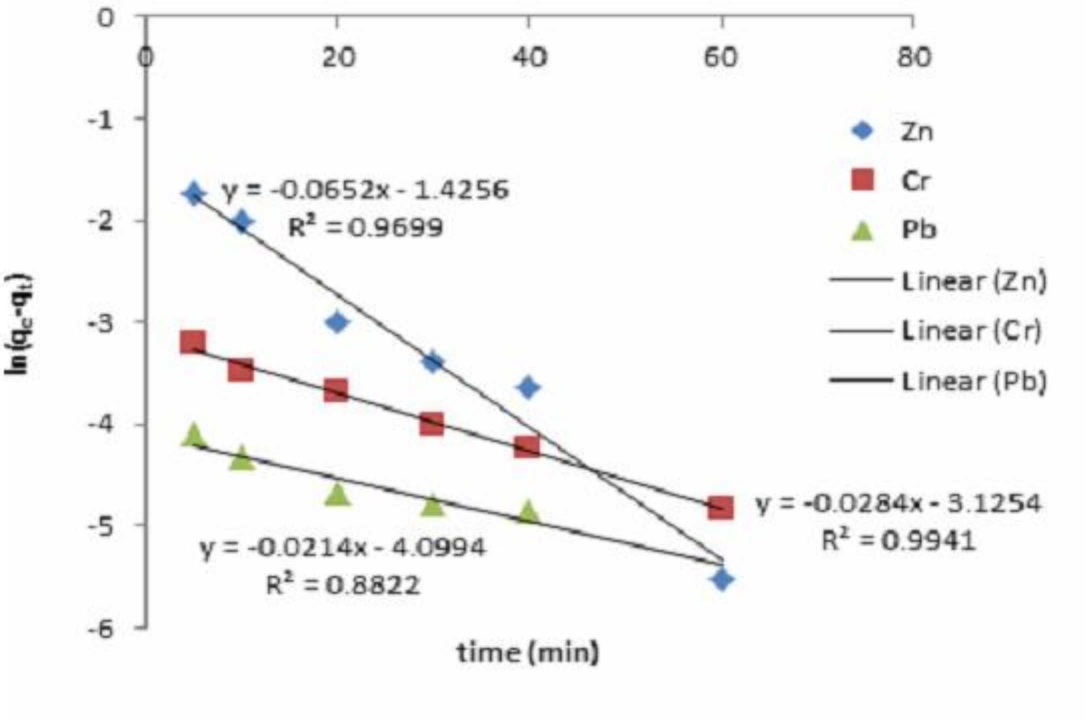

Figure.4. Pseudo-first-order reaction model for adsorption of Zn^{+2} ,Cr^{+6} and Pb^{+2} on adsorbent.

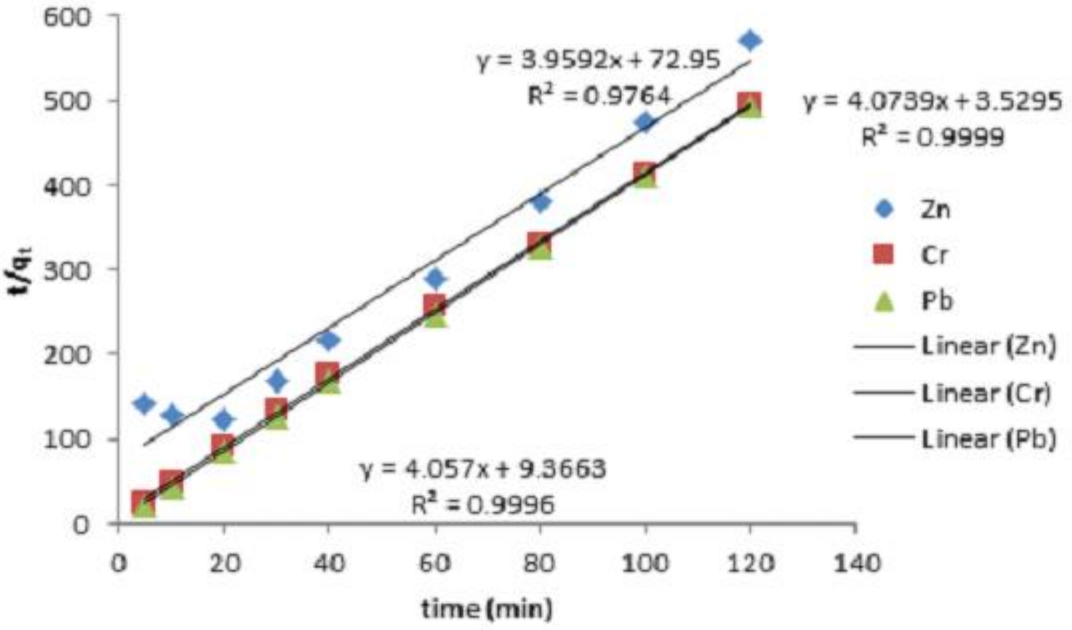

Figure.5. Pseudo-second-order reaction model for adsorption of Zn^{+2} ,Cr^{+6} and Pb^{+2} on adsorbent.

3.5 Adsorption isotherms:

The adsorption isotherm indicates how molecules of adsorbate are partitioned between the adsorbent and liquid phase at equilibrium as a function of adsorbate concentration. The Langmuir and Freundlich isotherms were fitted to the experimental adsorption equilibrium data for the single and multi-component systems. The Langmuir model assumes that adsorption occurs in a monolayer where the active sites are identical and energetically equivalent. The linear form of Langmuir isotherm equation is given as:

$$C_e/q_e = 1/q_{max}\, k_l + (1/q_{max})C_e$$

Where K_L is Langmuir equilibrium constant (l/mg), and q_{max} (mg/g) is the monolayer adsorption capacity. Both are determined from a plot C_e/q_e versus C_e (Fig.6).

Langmuir isotherm is frequently evaluated bya separation factor, R_L, which is defined as follows:

$$R_L = 1/\ 1+ (k_l * c_o)$$

Where: C_0 in this case is the higest initial solute concentration. The value of separation factor indicates the type of the isotherm and the nature of the adsorption process. Considering the RL value, adsorption can be unfavorable ($R_L<0$), linear ($R_L=1$), favorable ($0<R_L<1$) or irreversible ($R_L=0$) (Karagoz et al. 2008).

Freundlich isotherm is purely empirical and it best describes the adsorption on heterogeneous surfaces (Ng et al. 2002).

Freundlich isotherm equation is shown below in its linear form:

$$\text{Log } q_e = \log k_f + 1/n \log C_e$$

Where: K_F (l/g) and n (dimensionless) are the Freundlich adsorption isotherm constants, being indicative of the extent of adsorption and the degree of dependence between the solution concentration and adsorption, respectively. These parameters are determined from a plot log q_e versus log C_e (Fig.7). The parameters of these isotherms are shown in Table 3. The higher value of R^2 for Langmuir isotherm as compared to Freundlich isotherm for both mono- and multi-metal systems showed a better applicability of this model. This suggested that the adsorption of the metal ions occurs on a homogeneous surface by monolayer adsorption.

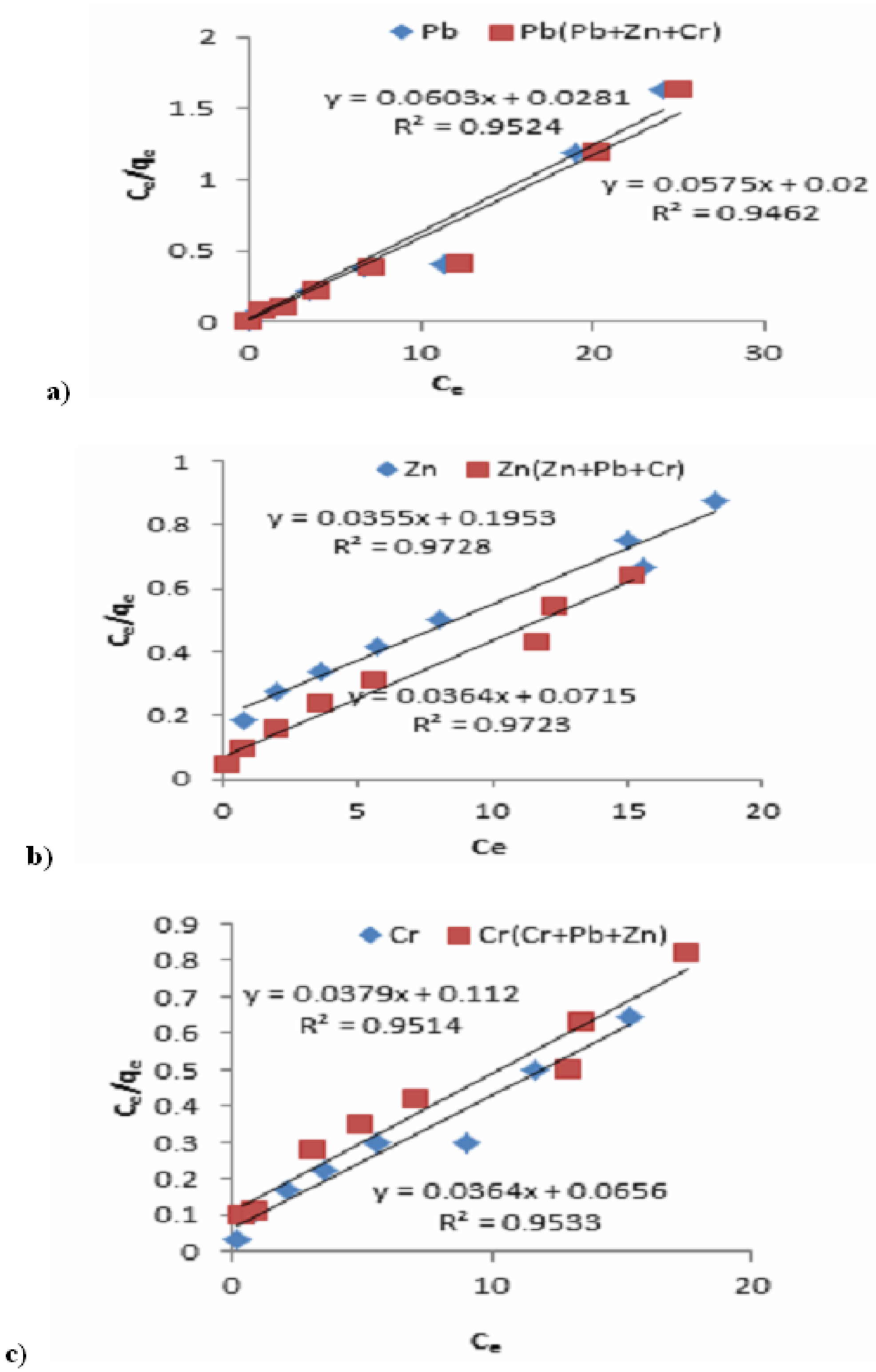

Figure 6. Langmuir adsorption isotherm for adsorption of **(a)** Pb^{+2}, **(b)** Zn^{+2} and **(c)** Cr^{+6}

in single and multi-component system .

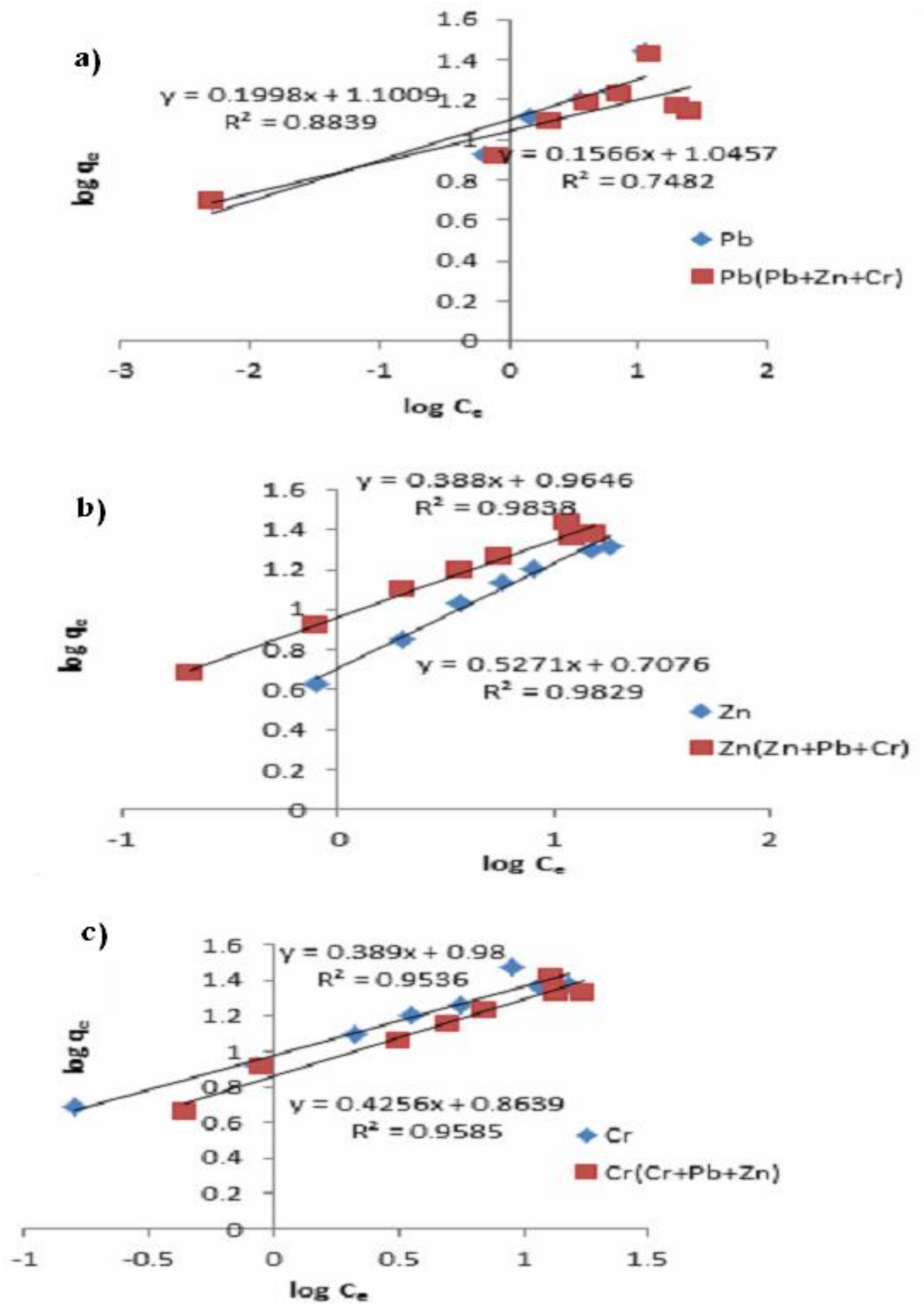

Figure 7.freundlich adsorption isotherm for adsorption of **(a)** Pb^{+2}, **(b)** Zn^{+2} and **(c)** Cr^{+6} in single and multi-component system.

Table 3. Langmuir and Freundlich isotherm parameters of single and competitive adsorption of $Pb^{+2,}$ Zn^{+2} and Cr^{+6} .

		Langmuir isotherm				Freundlich isotherm		
metal	**Adsorption systems**	**K_L (l/mg)**	**q_{max} (mg/g)**	**R_L**	**r^2**	**K_F (l/g)**	**n**	**r^2**
Pb^{+2}	**Pb^{+2}**	2.145	16.583	0.0115	0.9524	12.6153	5.005	0.8839
	Pb^{+2}+Zn^{+2}+Cr^{+6}	3.244	15.432	0.007	0.9471	11.10964	6.3856	0.7482
Zn^{+2}	**Zn^{+2}**	0.18177	28.169	0.12090	0.9722	5.10035	1.18971	0.9829
	Zn^{+2}+Pb^{+2}+Cr^{+6}	0.50911	27.472	0.0468	0.9723	9.21722	2.5773	0.9838
Cr^{+6}	**Cr^{+6}**	0.55487	27.472	0.043	0.9533	9.5499	2.570	0.9536
	Cr^{+6}+Pb^{+2}+Zn^{+2}	0.33867	26.38522	0.06874	0.9514	7.3097	2.3496	0.9585

3.6 Multicomponent system:

The results of the experiment are presented in Fig. 8. The results showed that Pb removal was not effected by any of the other cations, however, the presence of co-ions enhanced Zn removal but decreased Cr removal. In the presence of co-ions in solution, chemical interactions between the ions themselves, as well as with the biomass, take place resulting in site competition (Sommers, 1963; Khovrychev, 1973). Many of the functional groups present on the cell wall and the membrane are nonspecific and different cations compete for the binding sites. It has been reported that metal removal is increased as the ionic radii of metal cations affect the ion exchange and adsorption process (Marcus and Kertes, 1969). The differences in the sorption affinities may also be attributed to differences in the electrode potentials of the various ions. The greater the electrode potential, the greater is the affinity for biomass (Mattuschka and Straube, 1993). The ionic radii and the electrode potentials of the metal ions are summarized in Table 4. In multicomponent systems, the complex interactions of several factors such as ionic charge, ionic radii and electrode potential will account for the differences in the metal removal capacity of marine fouling.

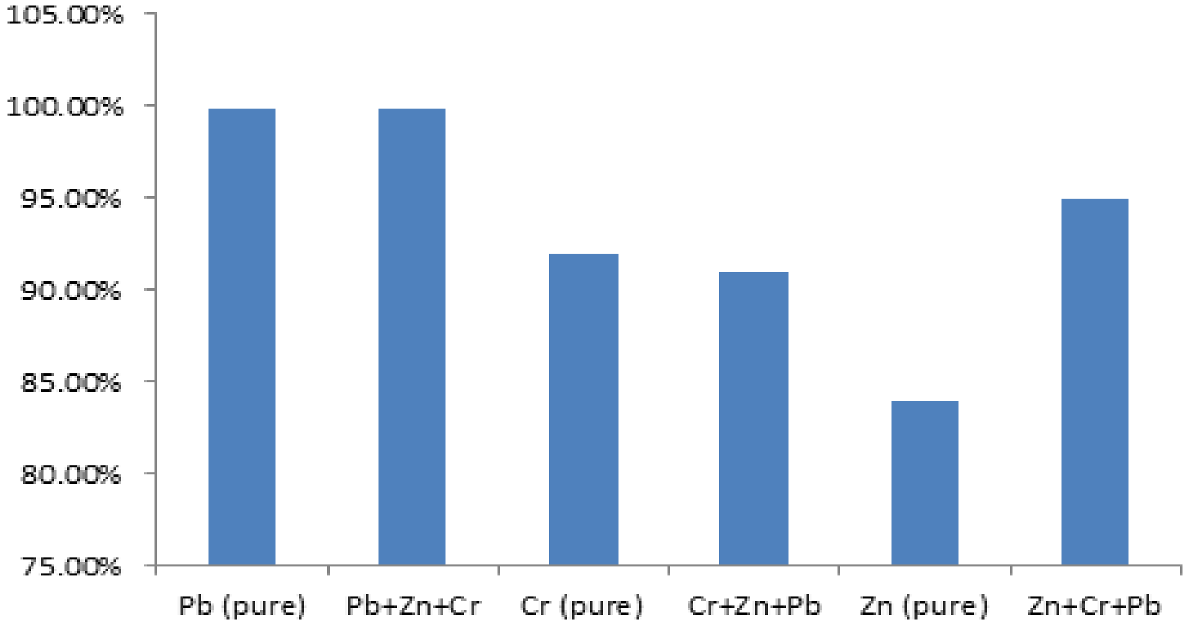

Figure 8. Effect of multi-component system on metal removal; concentration of metal ions: 5ppm; volume of solution: 50 ml; pH: Pb + Zn + Cr = 4.0; adsorbent loading: 1.0 g.

Table. 4. Ionic charge, ionic radii and electrode potentials of metal ions

Metal ion	Ionic charge	Ionic radii (A°)	Electrode potential (v)
Pb^{+2}	+2	1.32	0.126
Zn^{+2}	+2	0.74	0.763
Cr^{+3}	+3	0.64	0.744

3.7. *Application to leather tanning factory wastewater:*

Marine fouling was used for removing metal ions from leather tanning factory and the results are showed in Table 5. The pH of the wastewater was adjusted to a value 4 according to the experimental results. It can be observed that the concentrations of Pb^{+2}, $Zn^{+2}$and Cr^{+6} were reduced from 5.012 to 0.007 mg L^{-1}, 5.102 to 0.347 mg L^{-1} and 7.681 to .945 mgL^{-1},respectively. Generally, the removal percentages obtained were 99.9% for Pb^{+2}, 90% for Cr^{+6}, 93% for Zn^{+2}. The removal percentages for all the metal ions were listed in Table 5 and generally, it was indicated clearly that marine fouling has a high removal capability towards heavy metal ions.

Table 5. Removal of heavy metal ions from leather tanning factory wastewater by marine fouling

Metal ions	**Concentration (ppm)**		**Removal (%)**
	Initial	**After treatment**	
Pb^{+2}	5.012	0.007	99.9%
Zn^{+2}	5.102	0.347	90%
Cr^{+6}	7.681	0.945	93%

4. Conclusion

From the obtained results, it is evident that marine fouling is a good adsorbent for removal of lead, chromium and zinc ions from single and multi-component systems. Batch experiments were showed that ,pH of solution, contact time, initial Pb^{+2},$Zn^{+2}$and Cr^{+6} concentration and adsorbent dose are effective on the adsorption efficiency of Pb^{+2},$Zn^{+2}$and Cr^{+6}.The adsorption of heavy metal ions followed the Langmuir isotherm both in single and multicomponent systems, indicating that the sorption mechanisms did not change under conditions of competition. The results show that pseudo-second-order mechanism is predominant and that chemisorption might be the rate-limiting step that controls the adsorption process. Marine fouling successfully managed to remove heavy metal ions from real wastewater. Marine fouling is inexpensive and readily available, thus this study provide a cost effective means for removing metal ions from contaminated water or effluents.

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