Chromium and Iron Removal for Hard Chrome Bath Recycling using Eggshell Sorbent

Theeraporn Rubcumintara

Abstract—**This research is to study the removal of chromium and iron from spent hard chrome plating solutions using eggshell as selected bio-waste sorbent. It was found from the batch experiments that the chemically modified eggshell with hydrochloric acid resulted in better performance in comparison with the unmodified eggshell. The removal efficiency as well as adsorption capacity for Fe(II), Cr(III), and Cr(VI) were 95%, 100%, 13% and 94.5 mg/g, 18.8 mg/g, 173.4 mg/g, respectively in 48 h. The kinetics of chromium and iron sorption were described by pseudo first order and pseudo second order kinetic models. The experimental kinetic data fitted well with the pseudo second order kinetic model for both chromium and iron. The adsorption isotherms using Langmuir and Freundlich models were also evaluated by linearized forms. The best-fitted model to the experimental equilibrium data for eggshell sorbent was found to be the Freundlich model. From this investigation, the purification and recovery of hard chrome bath from spent plating solutions can be achieved using eggshell adsorption.**

Index Terms—**Hard chrome, recycling, eggshell, biosorbent.**

I. Introduction

At present, there are more than 400 companies registered as the manufacturer for hard chrome plating product in Thailand. Hard chrome plating is chromium plating that has been applied as heavy coating for wear resistance, lubricity, oil retention, and other wear purpose. Iron and steel are usually the items applied for hard chrome plating. The main component in hard chrome plating solution is chromic oxide (CrO_3) dissolved in water, and sulfate ion (SO_4^{2-}) introduced as sulfuric acid is a necessary catalyst in this chromium plating solution. These chromium acid solutions after a period of using in electroplating contain many impurities such as Cr(III), Cu(II), Fe(II) and Ni(II) [1]. These contaminants at high concentration will affect the plating efficiency as well as coating properties. As a result of bath contamination, the solutions which called spent bath must be disposed of. The recycling of these spent chromium baths then become more interest in terms of environment and economics. Much research has been done to remove chromium and other metals from rinse water, and biosorption as the method for metal binding using biomass from animal or plants has been proposed recently [2]-[14]. The availability as well as cost effectiveness of biomass materials cause biosorption become a potential alternative method. On the other hand, the research on removal and recovery of chromium from spent solutions has rarely been seen [1]. To purify and recycle spent hard chrome solutions, metal ion impurities must be removed. This work then aimed to gain more information about the recycling of spent hard chrome solutions by the removal of generated metal ion contaminants: Fe(II) and Cr(III). Biosorption onto eggshells sorbent was selected as an effective as well as economic method for metal ions removal in this study.

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II. Experiental

A. Materials

Spent hard chrome plating solutions used in this work is belongs to Siam Hard Chrome Company Ltd located at 37/134 Moo 9, Soi Nuantong, Setthakit Road, Suan Luang district, Kratumbaen, Samut Sakhon 74110. The average concentrations of Cr(III), Cr(VI) and Fe(II) in spent bath solutions were analyzed to be 3.77, 263.81 and 20.5 g/L, respectively.

B. Biosorbent Preparation

The hen eggshell used for biosorbent preparation were collected from Salaya Canteen, Mahidol University, Nakhonpathom. The shells were washed with distilled water several times to remove dirt and contaminants and dried in the oven. After drying, the shells become small pieces and were directly used in experiments. Some portion of dried eggshell were crushed using pestle and mortar and the particle size of +40, -40+70, -70+100 and -100 mesh or in the range from 125 to 500 μm were prepared to study the effect of particle size in comparison with the uncrushed dried shell. Besides the effect of surface modification to adsorption capacity was also investigated. The modified surface of uncrushed eggshell was prepared by soaking with hydrochloric acid solution for ten minutes then washed with distilled water to get neutral and dried in the oven.

C. Biosorption Experiments

Batch experiments for biosorption were conducted using 250 mL Erlenmeyer flasks containing 50 mL of spent chromium solutions and 10 g of dried eggshells at room temperature. When the time was reached, the reaction mixture was filtered to stop reaction. The filtrate were analyzed for trivalent and hexavalent chromium by titration method and for iron (II) content by UV-vis spectrophotometric method [*x*, *x*]. The adsorption capacity of Fe(II), Cr(III), and Cr(VI) onto eggshells both with and without acid treatment at time *t* was calculated by equation 1 and at equilibrium by equation 2 :

$$q_t = \frac{(C_i - C_t)V}{W} \tag{1}$$

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$$q_e = \frac{(C_i - C_e)V}{W} \quad (2)$$

where q_t and q_e is the metal uptake or loading capacity (mg/g) at time *t* and at equilibrium; C_i , C_t and C_e are the metal concentration at initial time, at time *t* and at equilibrium (mg/L), respectively; V is the solution volume (mL); and W is the sorbent dosage (g). The efficiency of metal removal was determined using equation 3 :

$$\%\,\mathrm{Re}moval = \frac{(C_i - C_t)\times 100}{C_i} \quad (3)$$

The Langmuir and Freundlich isotherms as shown in equation 4 and 5 were chosen for the estimation of metal adsorption. The linearized equations for Langmuir and Freundlich models were expressed as equation 6 and 7.

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (4)$$

$$q_e = K_f\, C_e^{\frac{1}{n}} \quad (5)$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{K_L q_{\max}} \quad (6)$$

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (7)$$

where $q_{\max}$ indicates the monolayer adsorption capacity of adsorbent (mg/g); K_L and K_f are the Langmuir constant (L/mg) and Freundlich constant (mg/g), respectively and n is the Freundlich exponent related to adsorption intensity (dimensionless).

D. Biosorption Kinetics

The kinetics studies were established similar to batch experiments but with various time interval from 0-72 h.

III. Results and Discussion

A. Effect of Biosorbent Concentration

The adsorption of Fe(II), Cr(III), and Cr(VI) using various amount of unground eggshells from 5-35 g was investigated with the 50 mL of solution volume at 25 °C for a period of 72 h. The percentage of Fe(II), Cr(III), Cr(VI) removal as a function of time and at equilibrium of 72 h were shown in Fig. 1- Fig. 4. It was found that the adsorption of Fe(II), Cr(III), and Cr(VI) increases with time and then stable at equilibrium for each concentration as seen in Fig. 1- Fig. 3. From Fig. 4, the sharp increase of metal removal was observed for 5-10 g of biosorbent dosage and then slightly increased when using 15-35 g of biosorbent. The removal of Fe(II), Cr(III), Cr(VI) was increased from 87.2, 82.8, 24.2 to 94.0, 100, 36.7%; respectively for an increase in eggshell dosage from 10 to 35 g at 25 °C and 72 h. The increase of percentage removal is due to increasing biosorbent surface area [9].

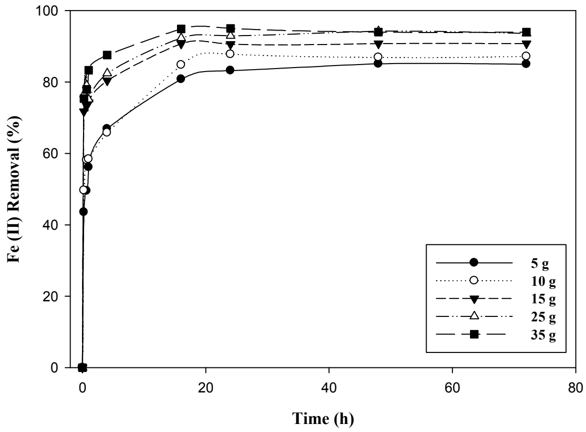

Fig. 1. % Fe(II) removal by uncrushed eggshells (T = 25 °C, C_i = 20.50 g/L, solution volume = 50 mL, time = 0-72 h)

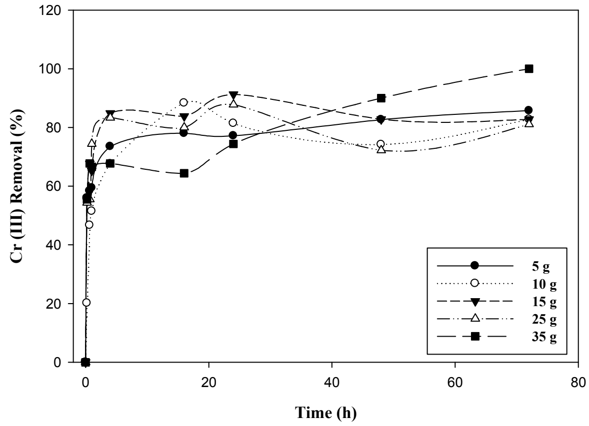

Fig. 2. % Cr(III) removal by uncrushed eggshells (T = 25 °C, C_i = 3.77 g/L, solution volume = 50 mL, time = 0-72 h)

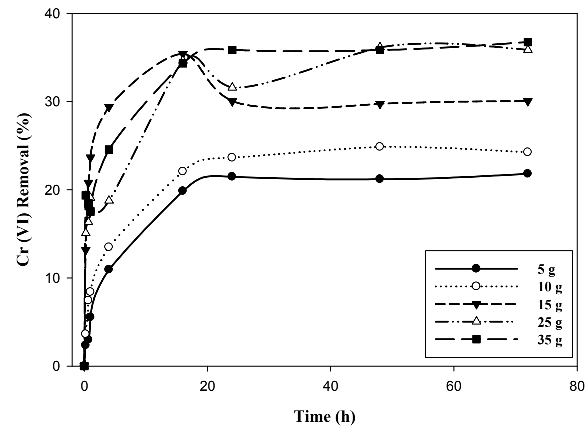

Fig. 3. % Cr(VI) removal by uncrushed eggshells (T = 25 °C, C_i = 263.81 g/L, solution volume = 50 mL, time = 0-72 h)

B. Effect of Biosorbent Particle Size

The effect of different biosorbent particle size on percentage removal of Fe(II), Cr(III) and Cr(VI) was observed and shown in Fig. 5- Fig. 7. The adsorption of Fe(II), Cr(III), and Cr(VI) on eggshell biosorbent decreases from 96, 100, 54.5 to 87.2, 82.8, 24.2 %; respectively with the increased particle size from 125 µm to 500 µm and uncrushed eggshell at 25 °C and 72 h. This is due to the fact that the surface area of small biosorbent particle size is higher than the large particle size which resulted in the higher percentage of adsorption.

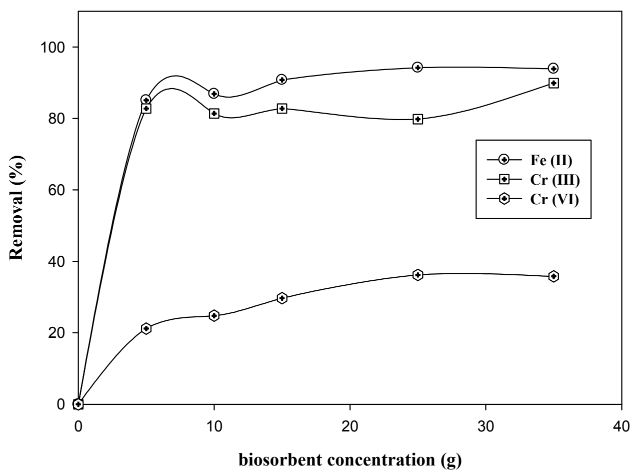

Fig. 4. Effect of sorbent dosage on Fe(II), Cr(III) and Cr(VI) removal by uncrushed eggshells (T = 25 °C, C_i = 20.5, 3.77 and 263.81 g/L for Fe(II), Cr(III) and Cr(VI), solution volume = 50 mL, time = 0-72 h)

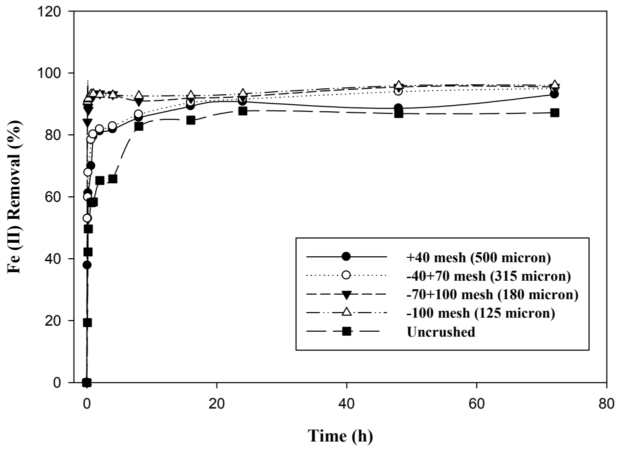

Fig. 5. Effect of eggshell particle size on Fe(II) removal (T = 25 °C, C_i = 20.50 g/L, W = 10 g, solution volume = 50 mL, time = 0-72 h)

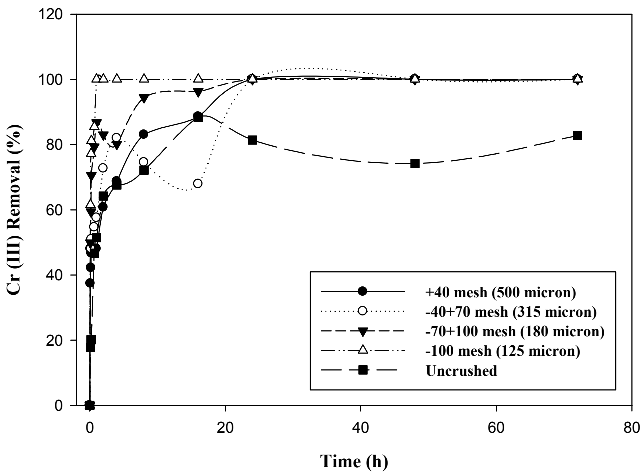

Fig. 6. Effect of eggshell particle size on Cr(III) removal (T = 25 °C, C_i = 3.77 g/L, W = 10 g, solution volume = 50 mL, time = 0-72 h)

C. Effect of acid Treatment on Eggshell Surface

The effect of uncrushed eggshells with and without acid treatment on percentage removal of Fe(II), Cr(III) and Cr(VI) was investigated as shown in Fig. 8. It was found from the results that the percentage removal of Fe(II) slightly increases from 87.5 to 88.6%, and Cr(III) removal was observed to increase from 82.7 to 100 % where as Cr(VI) removal decreases from 24.2 to 13 % at 72 h. This shows that the acid treatment on eggshells surface has specific effect to chromium adsorption. It was found from BET characterization on eggshell surface that the pore size on eggshell surface increases from 241.6 to 248.7 Å for eggshells with and without acid treatment, respectively. The increasing of Cr(III) removal may be due to the intra-pore diffusion mechanism and the higher mobility of the Cr(III) ions toward the eggshell surface in comparison with Cr(VI) ions [10]. According to the higher mobility the higher concentration of Cr(III) ions on the pore surface as well as the limitation of active sites at equilibrium (72 h), the percentage of Cr(VI) removal is then decreased from 24.2 to 13 % whereas Cr (III) removal was increased from 82.7 to 100 %.

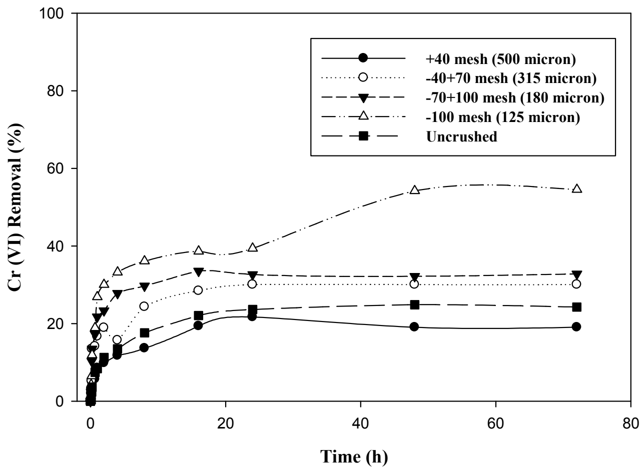

Fig. 7. Effect of eggshell particle size on Cr(VI) removal (T = 25 °C, C_i = 263.81 g/L, W = 10 g, solution volume = 50 mL, time = 0-72 h)

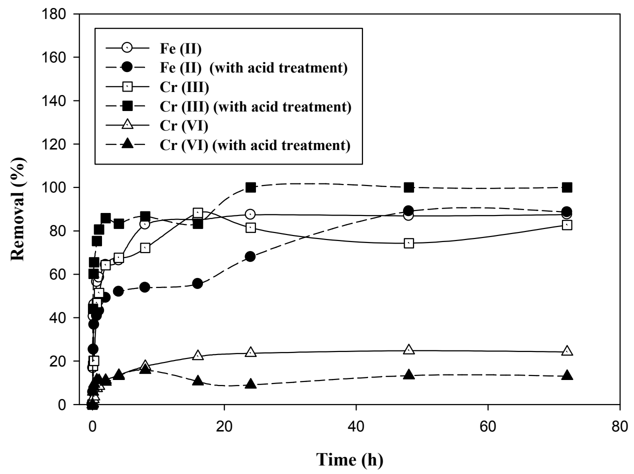

Fig. 8. Comparison of uncrushed eggshells with and without acid treatment on Fe(II), Cr(III) and Cr(VI) removal (T = 25 °C, C_i = 20.5, 3.77 and 263.81 g/L for Fe, Cr(III) and Cr(VI), W = 10 g, solution volume = 50 mL, time = 0-72 h)

D. Biosorption Equilibrium

The equilibrium biosorption of Fe(II), Cr(III) and Cr(VI) on the eggshells as a function of time is shown in Fig. 8 and

Fig. 9. From the experimental results, the adsorption onto eggshells with and without acid treatment reached equilibrium in 48 h. The percentage removal of Fe(II), Cr(III), and Cr(VI) were 89.2%, 100% and 13.3%, respectively. As shown in the Fig.9, the adsorption capacity for Fe(II), Cr(III), and Cr(VI) on eggshell surface was found to be 173.4, 18.8 and 94.5 mg/g, respectively. Moreover, the total concentration of Cr(III) and Fe(II) after adsorption was less than 15 g/L which is the criterion for standard hard chrome plating solutions. This means that it is possible to recycle spent hard chrome solutions with the 13 % loss of Cr(VI).

E. Biosorption Isotherm

The Langmuir and Freundlich isotherm models were applied to the experimental equilibrium data at 72 h for Fe, Cr(III), and Cr(VI) adsorption. From linear plots using equation 6 and 7, the corresponding linear regression correlation coefficient value, r^2 are given in Table I. From Table I, the r^2 values from Freundlich model were higher, ranging from 0.900-0.949. The Freundlich isotherm was then found to be the best-fitting isotherm.

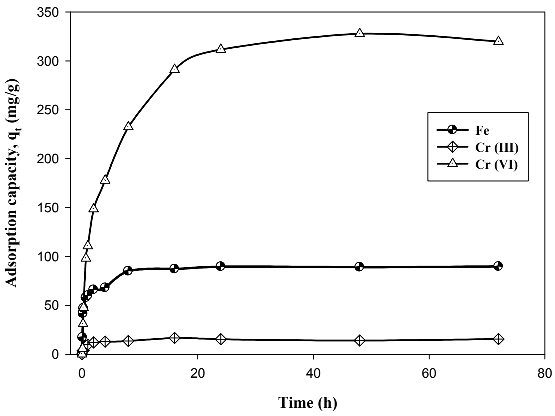

Fig. 9. Effect of contact time on Fe(II), Cr(III) and Cr(VI) loading capacity by uncrushed eggshells (T = 25 °C, C_i = 20.5, 3.77 and 263.81 g/L for Fe, Cr(III) and Cr(VI), W = 10 g, solution volume = 50 mL, time = 0-72 h)

TABLE I: LINEAR REGRESSION ANALYSIS

Isotherm	Correlation coefficient value; r^2		
	Cr (III)	Fe(II)	Cr(VI)
1. Langmuir	0.531	0.792	0.858
2. Freundlich	***0.924***	***0.949***	***0.900***

F. Biosorption Kinetics

Kinetic information for metal ion loading is important for designing batch adsorption system. The kinetics of the adsorption data was analyzed using two kinetic models, namely pseudo-first order and pseudo-second order kinetic model as shown by equation 8 and 9, respectively. Their linearized forms of pseudo-first order and pseudo-second order were derived as equation 10 and 11.

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \tag{8}$$

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{9}$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{10}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{11}$$

The data from dosage experiments were used to determine r^2 values and rate constant for pseudo first order and pseudo second order model as shown in Table II and Table III. Besides the good straight line for pseudo second order in comparison with pseudo first order was shown in Fig. 10 and Fig. 11. The higher r^2 values confirm that the adsorption data are well explained by pseudo second order kinetics, the adsorption in this study is then well supported to be chemisorptions [10]. The adsorption capacity for these metal ions can be estimated from equation 12-14.

TABLE II: LINEAR REGRESSION ANALYSIS AND RATE CONSTANT OF PSEUDO-FIRST ORDER EQUATION

Dosage (g)	Correlation coefficient value; r^2			k_1 (/min)		
	Cr(III)	Iron	Cr(VI)	Cr(III)	Iron	Cr(VI)
5	0.646	0.554	0.562	0.003	0.005	0.002
10	0.348	0.587	0.571	0.018	0.031	0.004
15	0	0.518	0.189	0	0	0.004
25	0	0.558	0	0	0.001	0
35	0	0.423	0.516	0	0.001	0.051

TABLE III: LINEAR REGRESSION ANALYSIS AND RATE CONSTANT OF PSEUDO-SECOND ORDER EQUATION

Dosage (g)	Correlation coefficient value; r^2			k_2 (g/mg min)		
	Cr(III)	Fe(II)	Cr(VI)	Cr(III)	Fe(II)	Cr(VI)
5	0.998	0.999	0.998	2.1×10^5	711.9	115.1
10	0.995	0.999	0.998	1.5×10^4	711.9	54.3
15	0.999	1.000	0.998	-4.8×10^4	247.2	-2.3
25	0.994	0.999	0.997	-7.7×10^3	271.4	14.3
35	0.981	0.999	0.999	4.4×10^5	111.7	9.0

$$\text{Fe(II)}: \quad \frac{t}{q_t} = 0.027 + 62.5\,t \tag{12}$$

$$\text{Cr(III)}: \quad \frac{t}{q_t} = 0.282 + 10.75\,t \tag{13}$$

$$\text{Cr(VI)}: \quad \frac{t}{q_t} = 0.164 + 2.5\,t \tag{14}$$

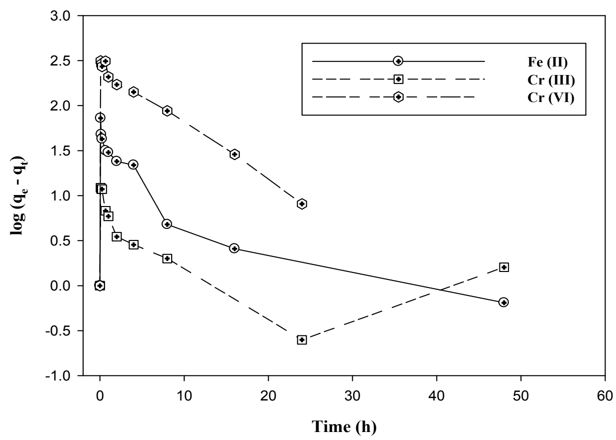

Fig. 10. Pseudo first order adsorption of Fe(II), Cr(III) and Cr(VI) by uncrushed eggshells without acid treatment (T = 25 °C, C_i = 20.5, 3.77 and 263.81 g/L for Fe(II), Cr(III) and Cr(VI), W = 10 g, solution volume = 50 mL, time = 0-72 h)

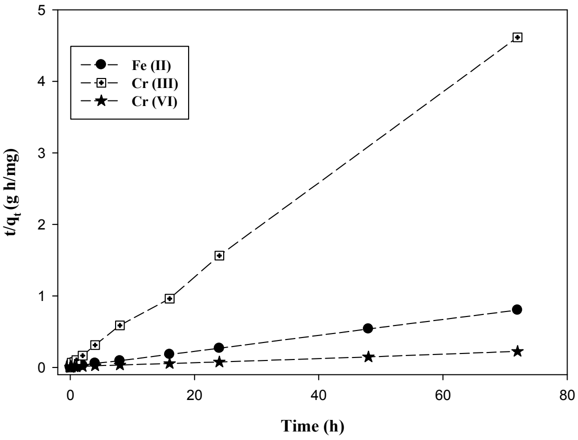

Fig. 11. Pseudo second order adsorption of Fe(II), Cr(III) and Cr(VI) by uncrushed eggshells without acid treatment

(T = 25 °C, C_i = 20.5, 3.77 and 263.81 g/L for Fe(II), Cr(III) and Cr(VI), W = 10 g, solution volume = 50 mL, time = 0-72 h)

IV. Conclusion

The uncrushed eggshell has been investigated as a cheap and effective biosorbent for the removal of Fe(II) and Cr(III) which are the major contaminants in spent hard chrome plating solutions having initial concentrations of Cr(III), Cr(VI) and Fe(II) equal 3.77, 263.81 and 20.5 g/L, respectively. From this work, 95 and 100% of Fe(II) and Cr(III), respectively can be removed with the 13 % loss of Cr(VI) from spent solutions. The sorption kinetics was found to follow the pseudo second order rate equation. The Langmuir and Freundlich adsorption isotherms were applied to equilibrium data and Freundlich isotherm was fitted better than Langmuir adsorption. The total concentration of Fe(II) and Cr(III) in spent plating solutions after adsorption was found to be less than 4 g/L. This showed that the feasibility to recover spent hard chrome solutions using waste biomass like eggshell is possible.

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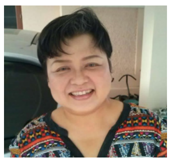

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