

## KINETIC STUDIES OF HEAVY METAL ION SORPTION BY MODIFIED OIL PALM WASTE MATERIAL

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### Abstract

Activated carbon adsorption has long been of beneficial use for numerous industries in order to achieve standard effluent discharge parameters. Owing to its high cost and difficult procurement of activated carbon, efforts are being directed towards finding efficient and low cost materials. Alternative utilization of oil palm waste materials, which is locally high in volume, is studied for adsorption of hexavalent chromium ion from aqueous solution simulating electroplating effluent. Simple chemical modification of oil palm waste materials has been made to enhance its adsorption capacity, thus preserving its economic value. Total removal of hexavalent chromium ions was achieved by oil palm fibre after being agitated for 2 hours under influence of acidic pH. Adsorption of chromium could be adequately described by both Freundlich and Langmuir isotherms. Kinetic studies were conducted using pseudo-first order and pseudo-second order kinetic models, yielding good  $R^2$  values from 0.9254 to 0.9870 and from 0.9936 to 0.9998 respectively. The analysis of variance (ANOVA) showed significant difference between the  $R^2$  values of the two models at 99 % confidence level.

Keywords: Oil palm waste material; Adsorption; Heavy metal ion.

### Introduction

Hexavalent chromium (Cr [VI]) is recognized as a human carcinogen [1]. Workers in many different occupations are exposed to hexavalent chromium. Occupational exposures occur mainly among workers who handle dry chromate-containing pigments, spray chromate-containing paints and coatings, operate chrome plating baths weld, cut or grind chromium-containing metals such as stainless steel. Conventional treatment; i.e. chemical reduction and precipitation normally cannot meet the stringent discharge limit as required by the authority.

Activated carbon adsorption has long been of beneficial use for numerous industries in order to achieve standard effluent discharge parameters. Owing to its high cost and difficult procurement of activated carbon, efforts are being directed towards finding efficient and low cost materials as alternative sources of adsorbent. Previous research include wood slab [2], coir pith [3], sphagnum moss peat [4], hazelnut-shell activated carbon [5] and wool, olive cake, pine needles, almond, charcoal and cactus leaves [6]. However, an adsorbent made of locally available agricultural or industrial wastes are of interest due to substantial reduction in cost aspect. Therefore, alternative utilization of oil palm waste materials, which is locally high in volume, is studied for adsorption of hexavalent chromium ion from aqueous solution simulating electroplating effluent. Simple chemical modification of palm fibre has been made to enhance its adsorption capacity, thus preserving its economic value.

### Experimental

#### Materials

Raw material used in the experiments was Malaysian oil palm fibre supplied by Palm Oil Research Institute of Malaysia (PORIM). Sulphuric acid treatment employed in the study was conducted according to Garg *et al.* (2004) in treatment of sawdust of Indian Rosewood, a timber industry waste to adsorb chromium from aqueous solutions. Potassium dichromate ( $K_2Cr_2O_7$ ), sulphuric acid ( $H_2SO_4$ ), sodium hydroxide (NaOH) and sodium bicarbonate ( $NaHCO_3$ ) were of analytical reagent grade and were used without further purification.

#### Procedures

Air-dried palm fibre was mixed with concentrated sulphuric acid in a ratio of 1:1 (w/w), and heated in a muffle furnace for 24 hours at 150°C. The material was then allowed to cool and thoroughly washed with distilled water, followed by soaking in 1%  $NaHCO_3$  solution to remove residual acid. The solid portion was dried in an oven for 24 hours at 105°C, and the resulting adsorbent was then used in the experiment without further sieving. Chromium (VI) solution was prepared using  $K_2Cr_2O_7$ , while pH was adjusted using 5N solutions of  $H_2SO_4$  and NaOH. Five sets of conical flasks were used in adsorption study; each filled with 500 mg adsorbent and 100 ml of 20, 50, 100, 150 or 200 mg/L of Cr (VI) solutions

respectively. The samples were agitated at 350 rpm using an orbital shaker to obtain kinetic data. The flasks were removed from the shaker for Cr analysis one after another at 10, 20, 40, 60, 90, 120, 150, 180, 210, 240, 270 and 300 minutes. Optimum pH for Cr (VI) adsorption was studied in preceding using 20 mg/L Cr (VI) and similar batch test

### Results and Discussion

High removal of hexavalent chromium ions was achieved by oil palm fibre after being agitated for 2 hours under influence of acidic pH (pH 1 to 2). At this pH range, the predominant Cr (VI) was  $\text{HCrO}_4^-$  [6,7], and therefore, electrostatic attraction occurred between the positively charged adsorbent and negatively charged  $\text{HCrO}_4^-$ . However, the decrease in Cr (VI) removal at higher pH values was apparently due to the competitiveness of another Cr (VI) species ( $\text{CrO}_4^{2-}$ ) and  $\text{OH}^-$  ions in the bulk [21]. pH 1.5 was adopted as optimum condition for further adsorption study rather than pH 1.0 to reduce chemical usage, and since total removal was not achieved at pH 2.

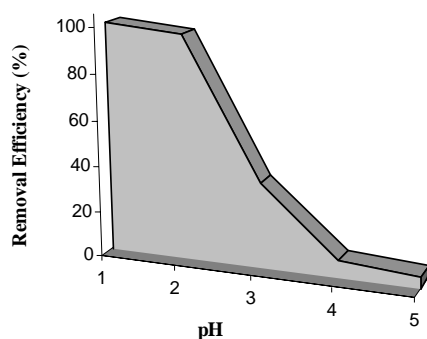


Figure 1: Effect of pH on the removal of Cr (VI) by oil palm fibre: [Cr (VI)] = 20 mg/L; volume, 100 ml; contact time, 2 h; agitation speed, 350 rpm; adsorbent dosage, 5 g/L; and temperature,  $28 \pm 1$  °C.

In the present study, two kinetic models are tested in order to predict the adsorption data of Cr (VI) as function of time using a pseudo-first-order and a pseudo-second-order kinetic model. Good  $R^2$  values were obtained from 0.9254 to 0.9870 and from 0.9936 to 0.9998 respectively (Table 1). The analysis of variance (ANOVA) showed significant difference between the  $R^2$  values of the two models at 99 % confidence level.

Table 1: Pseudo first order and pseudo second first order model constants

Initial Cr (VI) concentration (mg/L)	Pseudo first- order model		Pseudo second-order model	
	$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$k_2$ (g/mg.min)	$R^2$
20	0.0329	0.9631	0.0289	0.9998
50	0.0417	0.9254	0.0059	0.9991
100	0.0240	0.9350	0.0028	0.9991
150	0.0108	0.9772	0.0011	0.9955
200	0.0108	0.9870	0.0007	0.9936

Based on the high  $R^2$  values, it is concluded that adsorption of Cr (VI) onto the oil palm fibre can be describe by both models. Nevertheless, the  $R^2$  values also indicated that the sorption kinetics of Cr (VI) is better expressed by the second order reaction rates. Compliance to second order kinetic model strongly suggests chemical adsorption or chemisorption between the adsorbent and adsorbate.

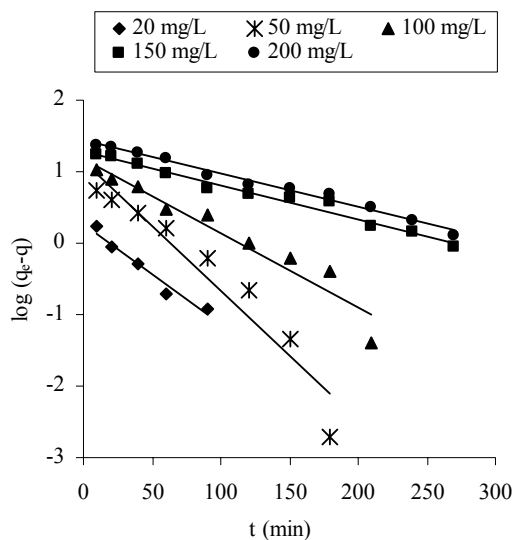


Figure 2: Pseudo first order kinetic plot at different initial concentrations: pH 1.5; volume, 100 ml; agitation speed, 350 rpm; adsorbent dosage, 5 g/L; and temperature, 28±1°C.

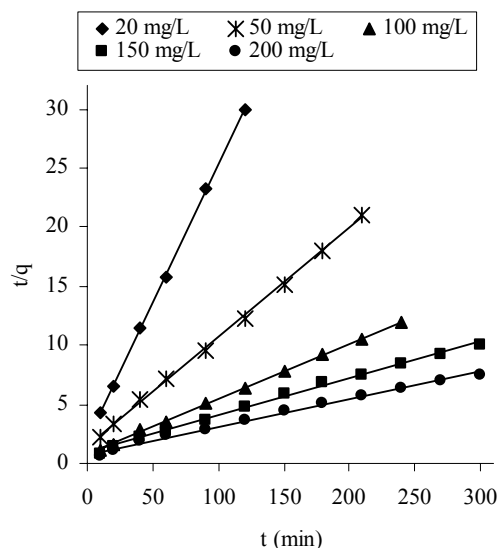


Figure 3: Pseudo second order kinetic plot at different initial concentrations: pH 1.5; volume, 100 ml; agitation speed, 350 rpm; adsorbent dosage, 5 g/L; and temperature, 28±1°C.

### Conclusions

pH values greatly influence Cr (VI) adsorption onto modified oil palm fibre, while adsorption of chromium (VI) could be adequately described by both pseudo-first order and pseudo-second order kinetic models.

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