

Kinetic study of Chromium VI adsorption onto palm kernel shell activated carbon

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Abstract. Heavy metal contamination of industrial effluent is one of the significant environmental problems due to their toxicity and its accumulation throughout the food chain. Adsorption is one of the promising methods for removal of heavy metals from aqua solution because of its simple technique, efficient, reliable and low-cost due to the utilization of residue from the agricultural industry. In this study, activated carbon from palm kernel shells has been produced through chemical activation process using zinc chloride as an activating agent and carbonized at 800 °C. Palm kernel shell activated carbon, PAC was assessed for its efficiency to remove Chromium (VI) ions from aqueous solutions through a batch adsorption process. The kinetic mechanisms have been analysed using Lagergren first-order kinetics model, second-order kinetics model and intra-particle diffusion model. The characterizations such as BET surface area, surface morphology, SEM-EDX have been done. The result shows that the activation process by ZnCl₂ was successfully improved the porosity and modified the functional group of palm kernel shell. The result shows that the maximum adsorption capacity of Cr is 11.40mg/g at 30ppm initial metal ion concentration and 0.1g/50mL of adsorbent concentration. The adsorption process followed the pseudo second orders kinetic model.

1. Introduction

Every year, a significant amount of heavy metals has been discharged into the environment as industrial wastes, causing serious soil and water pollution. Therefore, scientists have been focused on removal of these toxic materials. There are various procedures for removal of these toxic materials, such as ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electrodialysis [1]. Adsorption is one of the promising methods for removal of heavy metals from aqua solution. It is a simple technique, efficient, reliable and low-cost due to the utilization of residue from the agricultural industry [2].

The commonly used adsorbent in adsorption process is activated carbon, AC. This is due to its thermo-stability, large porous surface area, adjustable pore structure and size, cheap, ability to adsorb in aqueous or gaseous condition, affinity towards a broad type of organic and inorganic pollutants, and unique acid-base properties [3].

The common heavy metals which often polluted our mainstream are lead (Pb), cadmium (Cd), chromium (Cr), iron (Fe), nickel (Ni), copper (Cu) and zinc (Zn) which are the results of the industrial activity. Cr is toxic to human which will cause epigastric pain, nausea, vomiting, severe diarrhoea when entering the gastric system, corrosion of skin as well as respiratory tract and lungs cancer. It is often



used in leather tanning, electroplating, chromate preparation and metal finishing. The industrial limit on discharging Cr to the water bodies is 1ppm and the limit for potable water does not exceed 0.5ppm. Cr occurs in aqueous systems in trivalent and hexavalent forms. But the latter form is of particular concern due to its greater toxicity [4].

A kinetic study in adsorption process is important for the investigation of the adsorbent suitability as pollution control in a water system. It much depends on adsorbate-adsorbent interaction and the surrounding condition to evaluate its mechanism and reaction rate [5]. The kinetic models such as Langergren pseudo-first-order model, pseudo-second-order model, and Intraparticle diffusion model have been used to evaluate its adsorption rate and mechanism.

In this study, palm kernel shell, PKS from Sime Darby Plantation, Malaysia has been used for preparing the adsorbent by using chemical activation method. This research is focusing on the adsorption kinetic of chromium metal ions onto PKS activated carbon, PAC made from PKS ZnCl_2 activation.

2. Materials and methods

2.1 Process of producing adsorbent

The palm fruit obtained from the palm oil plantation area, Selangor, Malaysia, were crushed and the shells are separated. The collected shells were then brought for soaked in water for few hours and thoroughly washed with hot water to remove adhering dirt and soluble components. Cleaned shells are oven-dried at $85 \pm 10^\circ\text{C}$ until weight remains constant and finally crushed to gain smaller size.

The sample was activated by soaking in 500 ml of hot water and 100 g of ZnCl_2 in a beaker for 1 hour. Then, it was filtered and dried in the oven for 12 h at 80°C . Afterward, it was carbonized at 800°C for 1 hour in a programmable tube furnace (MTI Corp OTF-1200X, USA) at a flow rate of 500 ml/min of N_2 gas and heating rate of $10^\circ\text{C}/\text{min}$. In order to wash out the ZnCl_2 , the sample was soaked in 1M hydrochloric acid (HCl) solution that was heated to 80°C , rinsed with hot distillate water several times to washed-out ZnCl_2 . The PKS activated carbon, PAC was washed with distilled water until the pH exceeds 6 and dried in the oven for 24h at 80°C . Finally, it was sieved to obtained particular size e.g. 1.18-0.5mm, 0.5-0.25mm and 0.25mm using RETCH analytical sieve shaker (Germany) and keep in the airtight container.

2.2 Batch experiment

The adsorption experiment was performed by agitating of 50 mL Cr(VI) solution with 0.1g of PAC in a batch system using a laboratory shaker (LABWIT ZHWY-304, China) at 160rpm, $25 \pm 2^\circ\text{C}$ and pH6. Chromium stock solution of 1,000ppm was prepared by solving 2.83 g of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in 1L deionised water and diluted to the desired concentration level (2, 5, 10, 20, 30 and 50ppm).

2.3 Adsorption characterisation

The surface morphologies and elemental composition of PAC before and after adsorption of Cr were examined by using a field emission Scanning Electron Microscope, CARL ZEISS EVO MA10, UK. The specific surface area and pore size of PSH were measured using BET method by N_2 adsorption isotherm at 77K using a BET Micrometrics ASAP 2020, USA. BET and BJH methods will be used to calculate the surface area and the pore size distribution of PAC. The total volume of pores will be calculated at a relative pressure (P/P_0) of 0.99. The PAC was characterized by Fourier transform infrared (FTIR) Spectroscopy, (Thermo Scientific Nicolet 6700, USA) to analyze the organic functional groups present in the adsorbent.

2.4 Data analysis

Adsorption capacity, q_t ;
$$q_t = \frac{(C_i - C_t)V}{m} \quad (1)$$

Where, C_i (mg/l) C_t (mg/l) are the concentration in the solution at time $t = 0$ and at time t , V is the volume of solution (L) and m is the amount of adsorbent (g) added.

$$\text{Langergren pseudo first order model; } \log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (2)$$

$$\text{Pseudo second order model; } \frac{dq}{dt} = K_2(q_e - q_t)^2 \quad (3)$$

$$\text{Intra-particle diffusion model; } q_t = K_{id} t^{0.5} + C \quad (4)$$

Where, q_e is the adsorption capacity at equilibrium (mg/g), k_1 is the pseudo-first-order rate constant (1/min), k_2 (g/mg/min) is the pseudo-second-order rate constant of adsorption, $K_{id} t^{0.5}$ (mg/g min^{0.5}) is the rate constant of intra-particle diffusion and c is the intercept (mg/L).

3. Result and discussion

3.1 Characterization of PKS activated carbon

The microstructure of the PAC before and after the adsorption was observed as shown in figure 1. It shows significant changes in the structure of PKS after carbonization with zinc chloride. The activation process generates a highly porous morphology of PAC with different sizes of pores and shapes. The pore sizes of the PAC are ranged from about 1 to 30 μm . Similar morphologies are presented in the previous studies such as acid activated olive stone [6], char derived from sewage sludge [7].

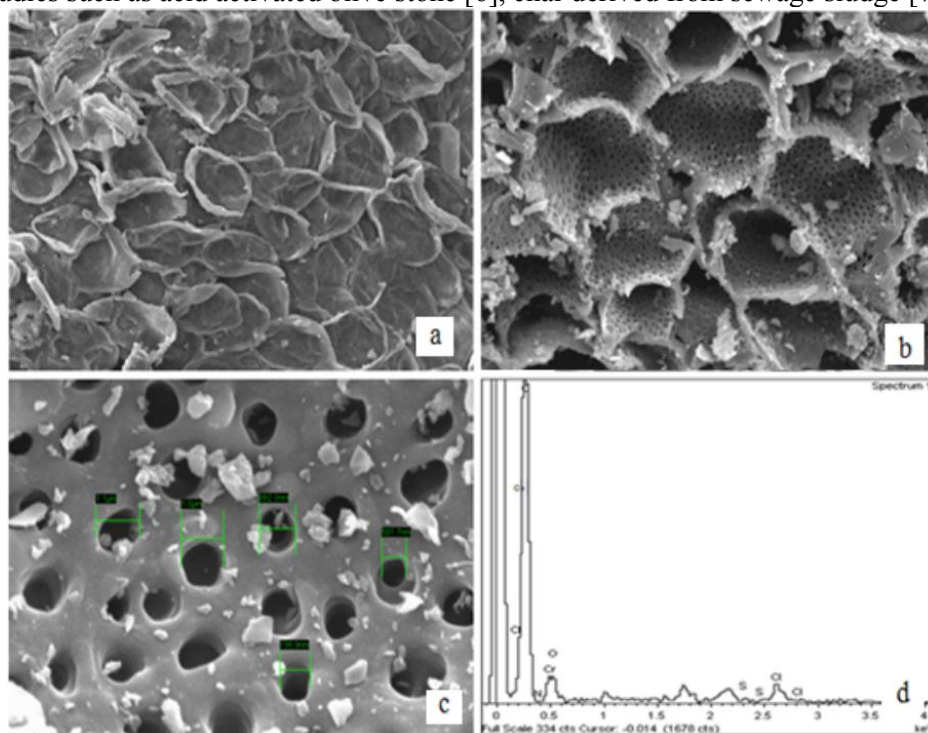


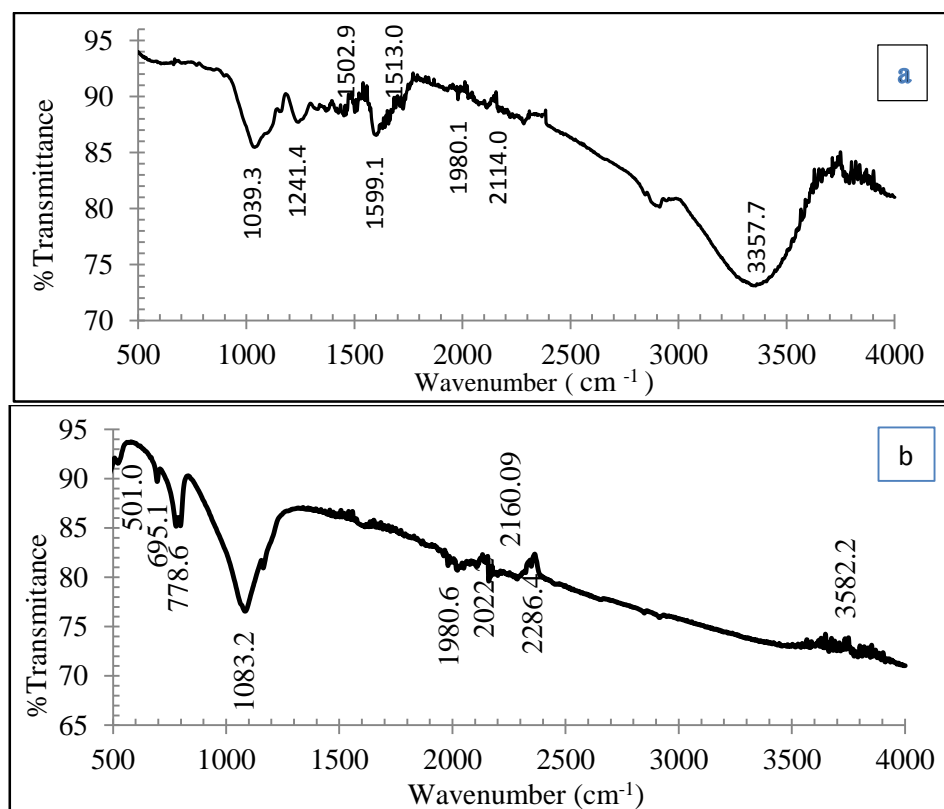
Figure 1. SEM image of; (a) 500 magnification for PKS (b) 1,000 magnification of highly porous structure of PAC (c) PAC after adsorption (magnification: 500), (d) EDX image after Cr(VI) adsorption

Summary of surface analysis is shown in **Error! Reference source not found.**, where it can be seen that BET surface area of PAC is comparable to the Jatropha activated carbon (JAC) developed by Masita et al. (2010) activation by ZnCl_2 and palm carbon (PC) and PAC developed by Wan Nik et al. (2006) activation by H_3PO_4 [8, 9]. In this research, specific surface area of PAC using ZnCl_2 is $839.21 \text{ m}^2/\text{g}$, which is higher than palm carbon ($500 \text{ m}^2/\text{g}$) and JAC ($186.12 \text{ m}^2/\text{g}$). This is on account of ZnCl_2 ability in creation pores into the inner structure of the adsorbent particle. The pore volume of PAC is $0.937 \text{ cm}^3/\text{g}$, which is higher than pore volume in PKS ($0.196 \text{ cm}^3/\text{g}$). Furthermore, PAC by 60.9% of the total surface area can be classified under micropore class.

Table 1. Surface area of PC, PAC (activation agent: ZnCl_2)

Parameters	Unit	PAC (ZnCl_2)
Specific surface area (Multipoint BET- N_2)	m^2/g	839.21
External surface area	m^2/g	327.29
Internal surface area	m^2/g	511.91
Average pore diameter	\AA	45.21
Total pore volume	cm^3/g	0.937

Activation with zinc chloride successfully removed most of originally presence functional groups. The main surface functional groups present in the derived PAC were Quinone and aromatic rings. The $\text{C} \equiv \text{O}$ stretching vibrations found was probably due to the incorporation of heteroatom (in this case, oxygen atom from enriched carbon dioxide atmosphere during the activation process) at the edge of the aromatic sheet or within the carbon matrix. Based on figure 2, during the carbonization process, most of the functional groups such as amines (1241.4-1599.1) and carboxylic acid (3357.7) were evaporated or removed.

**Figure 2.** FTIR, a. Palm Kernel Shell (PKS), b. Palm Activated Carbon (PAC)

3.2 Kinetics study of Cr metal ions removal using PAC

3.2.1 Effect of initial metal ions concentration

The kinetics study of heavy metal adsorption from wastewater is significant as it provides valuable information on the adsorption reaction pathways and its mechanism. The experimental results of adsorptions at various concentrations of 5-50 ppm, adsorption capacity at equilibrium (q_e) versus time for Cr is shown in figure 3. It shows that an increase in initial ions concentration was increased the adsorption capacity. At high concentration of Cr ion, the available sites of adsorbent still could adsorb

more adsorbate probably due to its high porosity and hence increased the percentage removal of metal ions. The adsorption capacity (qt) for each adsorbent was increased by increasing the metal ion concentration (equation 1). The adsorption capacity at equilibrium (qe) for Cr increased from 2.12 to 11.40 mg/g with an increase in the initial ion concentration from 5 to 50 mg/l and equilibrium is attained within 200 min.

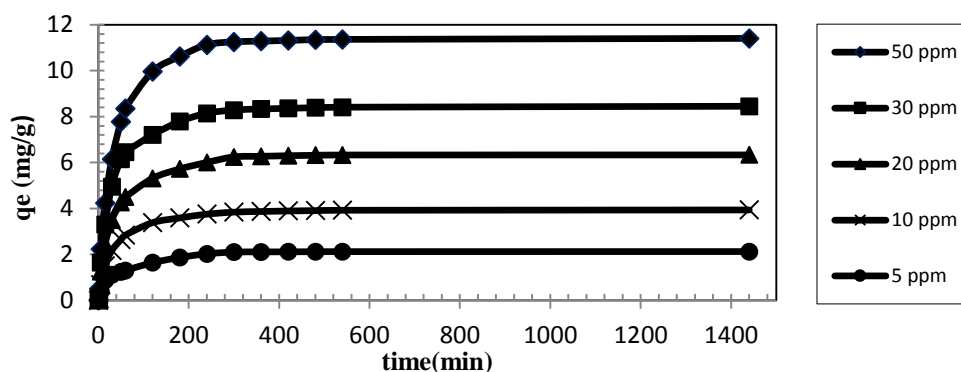


Figure 3. Effect of contact time on the adsorption of Cr ion onto PAC at different initial concentrations (Adsorbent size: 0.5 mm, dosage: 0.1g/50 ml, pH:6, temperature: 25°C, agitation speed: 160 rpm)

According to the graph, three consecutive mass transport steps are associated with the adsorption of solute from solution by the porous adsorbent. First, the adsorbate migrates through the solution, film diffusion, followed by a solute movement from a particle surface into the interior site by pore diffusion and finally the adsorbate was adsorbed into the active sites in the interior of the adsorbent particle. This phenomenon takes relatively long contact time. A similar phenomenon was observed for the adsorption of Cd from aqueous solution on activated carbon from jatropha seed [8].

3.2.2 Adsorption kinetic analysis

Three kinetic models had been utilized to analyse the kinetic mechanisms, Lagergren first-order kinetics model (equation 2), second-order kinetics model (equation 3) and intra-particle diffusion model (equation 4). The kinetic study is important since it measures the potential rate-controlling step and the transient behaviour of the metal ions adsorption process. All the kinetic parameters and correlation coefficients were tabulated in table 2. It shows the best fitting kinetic model is pseudo-second order kinetic model which approximately follow the multistep chemisorption process [8]. Figure 4 shows the linearized form of pseudo-second order and the value is calculated and tabulated in table 2.

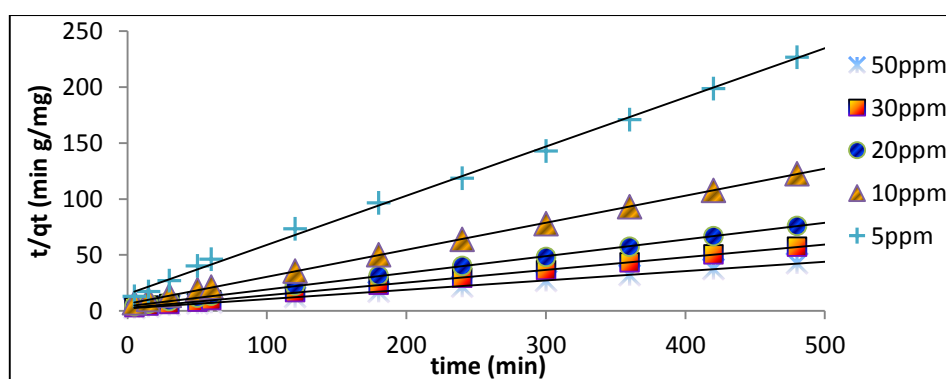


Figure 4. Pseudo-second-order kinetics for Cr(VI) adsorption at different initial metal ion concentration (Adsorbent size: 0.5mm, C_0 : 30ppm, pH:6, temperature: 25°C, agitation speed: 160rpm)

Table 2. Calculated kinetic parameter for the adsorption of Cr(VI)

System parameters	q_e (exp.)	Pseudo-first order kinetics			Second-order kinetics			Intra-particle diffusion		
		q_e (cal.)	K_1	R^2	q_e	K_2	R^2	K_{id}	C_i	R^2
5ppm(mg/L)	2.124	2.4254	0.012	0.977	2.215	0.014	0.989	0.009	0.590	0.998
10ppm(mg/L)	3.943	4.4187	0.012	0.963	4.159	0.0088	0.999	0.152	1.543	0.942
20ppm(mg/L)	6.336	7.1499	0.011	0.963	6.583	0.0058	0.999	0.239	2.481	0.956
30ppm(mg/L)	8.448	9.792	0.013	0.956	8.865	0.0047	0.999	0.288	3.885	0.928
50ppm(mg/L)	11.40	12.97	0.015	0.984	11.56	0.0033	0.999	0.464	4.326	0.932

Intra-particle diffusion data as shown in table 2 clearly confirm the mechanism of rate-limiting step. The intra-particle diffusion rate constant is calculated from the linear plot of qt vs $t^{1/2}$, where the value C is the intercept. The C value is to estimate the resistance or thickness of the boundary layer of adsorption [8]. From table 2, it proved that the thickness of the boundary layer of PAC into Cr are increasing from 0.590 to 4.326 mg/L. The increasing value of intra-particle diffusion constant, 0.009 to 0.464 mg/g min^{0.5} with the increasing metal ions concentration of 5ppm to 50ppm proved the rate-limiting step of adsorption of Cr onto PAC. The multilinearity of plots proved that the adsorption process takes place by more than one step. First, external macroporous and mesoporous diffusion, also known as bulk diffusion, followed by linear portion to intra-particle diffusion and finally, the flat plateau to equilibrium, where no more adsorption can happen due to the pores are fully employed.

4. Conclusion

The characterization of PAC shows that carbonization with ZnCl₂ has improved the surface area and its porosity, hence increased the adsorption capacity due to a high surface area. The chemical modification was proved to improve the adsorbent properties. The kinetic study shows that the adsorption follows pseudo-second order kinetic model which refers to chemisorption process with adsorption capacity of 11.40mg/g at 30ppm initial metal ion concentration.

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