Adsorption Isotherm of Chromium (VI) into \( \text{ZnCl}_2 \) Impregnated Activated Carbon Derived by Jatropha Curcas Seed Hull

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Abstract. Hexavalent chromium is carcinogenic and should be removed from industrial wastewater before discharged into water resources. Adsorption by using activated carbon from biomass is an economic and conventional way on removing the heavy metal ions from wastewater. In this research, activated carbon is synthesized from \textit{Jatropha curcas} L. seed hull through chemical activation with \( \text{ZnCl}_2 \) and carbonized at 800 \( ^\circ\)C (JAC/\( \text{ZnCl}_2 \)). The activated carbon has been characterized using FTIR, SEM-EDX, BET and CHNS-O analyzer. Adsorption isotherms have been analysed using Langmuir and Freundlich models to determine its removal mechanism. The maximum adsorption capacity of Cr (VI) metal ions onto JAC/\( \text{ZnCl}_2 \) activated carbon is 25.189 mg/g and following Langmuir isotherm model which is monolayer adsorption.

1. Introduction
Chromium exists in almost anywhere on earth, including seawater and plants, but its hexavalent state (+6) has been proven to be the most poisonous and carcinogenic to both human and animal [1]. Because of its high corrosion-resistant and hardness, chromium has been used in many metal industries, ranging from printing machine to aerospace manufacturing. Many researchers have tried other materials to replace this element in the industry but none of the materials can surpass the excellent layer quality and cost-effectiveness it holds [2]. Hexavalent chromium can be reduced to trivalent chromium that is insoluble in water and can be separated easily [3]. This reaction is manipulated by many of the removal techniques in industrial wastewater, including acidification with sulphuric acid, chemical reduction with sulphite sulphur compounds and neutralization with a sodium hydroxide solution. The other way is through a separation process such as ion exchange and membrane [4]. However, these methods produce a huge amount of sludge that will end up in the landfill, which creates another environmental concern [2]. Besides ion exchange and membrane separation techniques, adsorption method has attracted many attentions nowadays [5]. This is because of the ability to recover and reuse precious chromium that is adsorbed using activated carbon, instead of contributing to soil and river pollution by sending the waste sludge to landfills. Some of the materials that have been used as an adsorbent of chromium (VI) were marine algae, KNb3O8 compound and sol-gel hydrotalcite-like compounds [5, 6, 7]. Besides,
Shah et al. (2009) have combined both methods of reduction of Cr (VI) to Cr (III) with sorption using natural sorbent material to increase the efficiency of chromium removal [8]. Activated carbon is synthesized from carbonaceous materials, called the precursor that mutually affecting the adsorption performance of the produced activated carbon with its activation properties [9]. There are two types of activation method namely physical and chemical activations. Zinc chloride (ZnCl$_2$), being one of the most common chemicals used in chemical activation, has several reported advantages towards physical activation. Ahmadpour and Do [10] found that it can improve the pore creation and gives higher yield because the chemical retards tar escape during carbonization and endorses the condensation reaction. Mohanty et al. (2005) had also observed that ZnCl$_2$-activation increases BET surface area [10].

Since the material cost of activated carbon is high, activated carbons produced from a low-cost material such as biomass have brought special attention to researchers in order to develop a sustainable wastewater treatment in the industry [11, 12]. Tumeric waste, Ferronia shell, Delonix shell and Ipomea Carnia stem are among other biomass that have been studied and proven to have potentials of being activated carbon [13]. Esmaeili et al. (2010) have used algae as the precursor for the activated carbon to remove chromium from solution while Tangjuank et al. (2009) have used cashew nut shells [5,14]. Besides, Venkatraman et al. (2009) have produced low-cost acid-activated activated carbon from Borassus bark to adsorb chromium ions from metal solution [15]. Seed hull of Jatropha curcas L. or physic nut is one of many biomasses that can be used as a precursor. It is mainly produced from soap and medicine industry as well as the bioenergy production [16]. Many studies have been done to use a physic nut as a precursor of activated carbon, one of which is done by Namasivayam et al. (2007) where they used the husk to adsorb anions, heavy metals, organics and dyes from water [17]. Mohammad et al. (2010) studied the removal of cadmium and zinc ions from aqueous solution using a physic seed hull and concluded that it can be a potential low-cost adsorbent for the removal of metal ions [18]. This project synthesized activated carbon from jatropha seed hull by chemical activation technique with Zinc chloride (JAC/ZnCl$_2$). The JAC/ZnCl$_2$ has been utilized as an adsorbent for chromium ion removals from aqueous solutions. The experimental data were fitted to the Langmuir and Freundlich isotherm models to determine its isotherm mechanism. This research aim is to improve the surface area and porosity of jatropha seed hull by chemical activation, hence increase its adsorption capacity for chromium metal ions in aqueous solution. The modification was improved its surface area and reduce the pore size, consequently, improved it adsorption tendency and capacity as compared with research by Mohammad et al. (2010) [18].

2. Materials and Methods

2.1. Synthesis of Jatropha Activated Carbon

All chemical used were analytical grade and were obtained from Merck. Jatropha seed hull (JSH) was washed and soaked in 80°C water until clean. Then, it was dried in 80°C oven for 24 hours and later soaked in ZnCl$_2$ overnight. The ZnCl$_2$-activated JSH was dried before carbonized in MTI Corp OTF-1200X (USA) tube furnace at 10°C/min for 60 minutes at 800°C under Nitrogen flow. After cooled, they were drenched in 1 M HCl solution at 80°C and rinsed with distilled water until the pH becomes 6. Finally, JAC/ZnCl$_2$ is sieved and -0.5+0.25 mm sieve size of the particle is used as an adsorbent.

2.2. Characterization of Jatropha Activated Carbon

The characteristics of JAC/ZnCl$_2$ were observed and analyzed through its elemental composition, inorganic components, surface morphology, surface area, pore volume, porosity and surface functional groups. The elemental composition was analyzed using Thermo Fin 1112 CHNSO-Analyzer (Italy) and the inorganic components were examined in PANalytical Mini Pal 2 X-Ray Fluorescence (Netherlands). The surface morphology was studied using CARL ZEISS EVO MA10 Scanning Electron Microscope (UK). The surface area and the porosity characteristic were investigated using BJH method with BET Micromeritics ASAP 2020 (USA). The surface functional groups were detected using Thermo Scientific Nicolet 6700 Fourier Transform Infrared Spectroscopy (USA).
2.3. Adsorption Isotherm
The adsorption of chromium by JACZnCl$_2$ was carried out in a batch system. Chromium solution of 1,000 ppm was prepared by using 2.83 g of potassium dichromate, K$_2$Cr$_2$O$_7$ in 1 L distilled water. Then, aqueous solutions of 25 mL with the initial concentration in the range of 5 to 60 ppm were prepared from the 1,000 ppm solution. All batches were done with replicates in 100 mL beaker and capped with aluminum foil. They were also rotated on LABWIT ZHWY-304 (China) rotary shaker at 160 rpm after 0.1 g of adsorbent was added. Each sample taken is diluted to an appropriate ratio before being analyzed using Perkin Elmer Analyst 800 Atomic Absorption Spectrometer (USA).

2.4. Mathematical Models
Adsorption capacity, $q_t$

$$q_t = \frac{(C_0 - C_t)\nu}{m}$$  \hspace{1cm} (1)

where, $q_t$ is the amount of chromium adsorbed per gram of JAC/ZnCl$_2$ (mg g$^{-1}$), $C_0$ and $C_t$ are the initial and final chromium concentration in the solution for time $t$ (mg L$^{-1}$).

Adsorption capacity at equilibrium, $q_e$

$$q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e}$$  \hspace{1cm} (2)

$$q_e = K_F C_e^\frac{1}{n}$$  \hspace{1cm} (3)

Where, $q_e$ is the amount of chromium adsorbed per gram of JAC/ZnCl$_2$ at equilibrium (mg g$^{-1}$), $C_e$ is the chrom in the solution at equilibrium (mg L$^{-1}$), $q_{\text{max}}$ is maximum adsorption capacity (mg g$^{-1}$), $K_L$ is Langmuir constant that corresponds to adsorption energy (L mg$^{-1}$), $K_F$ is Freundlich constant that indicates the relative adsorption capacity (mg$^{1/(1/n)}$ L$^{1/n}$ g$^{-1}$), and $n$ is related to the intensity of adsorption. Equations (2) and (3) can be linearized into equations (4) and (5) respectively;

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{\text{max}}}\right) \frac{1}{C_e} + \frac{1}{q_{\text{max}}}$$  \hspace{1cm} (4)

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$  \hspace{1cm} (5)

Separation factor, $R_L$

$$R_L = \frac{1}{1 + K_L C_o}$$  \hspace{1cm} (6)

Where, $R_L$ is separation factor (dimensionless), $K_L$ is Langmuir constant (L/mg), and $C_o$ is the concentration of chromium in the bulk fluid (mg/L).

3. Results and discussion

3.1. Characterization of Jatropha Activated Carbon
The elemental analysis showed that carbon dominates by 65% of the weight of JAC/ZnCl$_2$, followed by oxygen, hydrogen and nitrogen with a composition of 31%, 3% and 1% respectively. These elements are bonded to carbon either as the basic structural units in the microtexture of the activated carbon or as surface functional groups when bonded at the edge of the aromatic sheets [19]. Figure 1 shows the magnified image of JAC/ZnCl$_2$ that was used for adsorption of chromium. Before adsorption, it can be seen that it has considerably good surface morphology because of the presence of natural pores, which gives a potential of being a good adsorbent. The three groups of pores in accord with the International Union of Pure and Applied Chemistry (IUPAC) are the macro, meso and micro that have more than 50 nm, between 2 to 50 nm, and less than 2 nm in diameter respectively [20]. All of these pores can be seen distributed all over the surface with some internal pores as the zinc-activation penetrated deeper into the body of the particles. Grinding the JAC/ZnCl$_2$ to the required size has broken up the external macro and meso-pores on the surface of the particles. These breakages put together the small pores into larger ones. Hence, opened the surface to the internal meso and micro-pores, and finally increasing the surface area which enhances the capacity of adsorption. After the adsorption, chromium ions can be seen attached to the surface of JAC/ZnCl$_2$. This is validated by Energy-Dispersive X-ray scanning in Figure 1(c) where chromium ions appear on its surface.
Surface area is crucial for an adsorption of adsorbate onto the surface of adsorbent, and the porosity of the particles contributes to the large extent in having a larger surface area as more pores to create the bigger surface area. BET surface area for JAC/ZnCl$_2$ is 667.16 m$^2$/g which is comparable to the Jatropha activated carbon developed by Xin-hui et al. (2010) using NaOH and Sricharoenchaikul et al. (2007) using KOH that are 1,350 and 532.3 m$^2$/g respectively [21, 22]. Micropores contribute 69% of the total surface area of JAC/ZnCl$_2$ but the average pore diameter of 2.2 nm locates JAC/ZnCl$_2$ under mesopore class. FTIR spectra of JSH and JAC/ZnCl$_2$ has been taken and its was proved the functional groups presence before the chemical activation that is at the surface of JSH, include amines, alkynes and carboxylic acids have been completely removed in this chemical activation using ZnCl$_2$.

3.2. Adsorption Isotherm Studies

The adsorption isotherm can be investigated from the correlation between the adsorption capacities of chromium on JAC/ZnCl$_2$ with the concentration of chromium in the aqueous solution, both at equilibrium. The adsorption of chromium on JAC/ZnCl$_2$ for time $t$ can be found from the concentration of chromium left in the solution at that time, which is shown in equation 1. Figure 2 shows the adsorption capacities of chromium for different initial concentrations against contact time until it reaches equilibrium. It shows the adsorption is increased by time and with the increment in initial metal ion concentration. It found that the equilibrium is attained at around 4 hours and followed the three-step kinetic process, starting with rapid uptake of metal ions, the uptake is slightly reduced after 20 minutes and finally, no more significant uptake which shows the pores are fully employed [18].

![Figure 2: Adsorption Isotherm Study of Chromium with JAC/ZnCl$_2$ at 25 °C](image)

Adssorption isotherm of chromium ions onto JAC/ZnCl$_2$ was investigated by fitting the experimental data into Langmuir and Freundlich isotherms that are described by equations 2 and 3 respectively. Equations 2 and 3 can be linearized into equations 4 and 5 respectively. Table 1 summarizes the values of Langmuir and Freundlich constants obtained from linearized equations of Langmuir and Freundlich isotherms. As Langmuir isotherm assumes that only one metal ion can be held by each site on the surface of adsorbent or monolayer adsorption, while Freundlich isotherm assumes that adsorption takes place on heterogeneous surfaces. Both $R^2$-values showed in Table 1 are considerably high and near unity, but Langmuir isotherm gave the best fit with the highest $R^2$-value. This suggests that the adsorption of chromium onto JAC/ZnCl$_2$ obeys Langmuir isotherm with maximum adsorption capacity, $q_{max}$ = 25.189 mg/g and the affinity of the binding sites and energy of adsorption, $K_L$ = 0.4148 L/mg. The dimensionless constant separation factor, $R_L$ is given by equation 6. The Langmuir isotherm is favourable if the value lies between 0 and 1, while values higher than unity suggest unfavourable
adsorption system. The separation factor for this system falls in the range of 0.04 to 0.33. These near-zero values depict the desired adsorption which confirms that this process is favourable [23].

Table 1: Values of Langmuir and Freundlich Constants for Adsorption of Chromium with JAC/ZnCl$_2$

| Adsorbate | Langmuir constants | Freundlich constants |
|-----------|--------------------|----------------------|
|           | $q_{\text{max}}$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $n$ | $K_F$ (L/mg) | $R^2$ |
| JAC/ZnCl$_2$ | 25.189 | 0.4148 | 0.9906 | 1.3060 | 6.6333 | 0.9803 |

The previous works of Mohammad et al. and Sen et al., 2010, used non-activated Jatropha seed hull to adsorb metal ions from wastewater also found Langmuir isotherm satisfied the adsorption mechanism with maximum adsorption capacity of 6.724 mg/g for Zn$^{2+}$ and 6.983mg/g for Cd$^{2+}$ [11, 23].

4. Conclusion

The JAC/ZnCl$_2$ obtained has an improvement compared to an untreated JAC in terms of its surface area, porosity and metal ion removal from wastewater. The adsorption is monolayer on the surface of the adsorbent with maximum adsorption capacity of 25.189 mg/g, which is higher compared to untreated JAC. The adsorbent produced will be tested for its affinity towards a different type of metal ions in future. This research would benefit for the removal of heavy metal from industrial wastewater such as electroplating, solar photovoltaic and etc. in order to save the environment.

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