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Removal of Chromium (VI) in Aqueous Solution by Charcoal Adsorbent derived PET Plastic Waste

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Abstract. This study was conducted to assess the potential of charcoal and activated charcoal derived Polyethylene Terephthalate (PET) as adsorbent through the experiment of chromium hexavalent [Cr (VI)] removal from aqueous solution. The study aims to investigate the optimum adsorption conditions for Cr (VI) removal in aqueous solution under diverse adsorption operating conditions, namely pH, contact time, agitation speed, adsorbent dosage, and initial concentration. The diameter of the charcoal produced was 600 μm. The results showed that 80 % and 90 % of Cr (VI) removal were achieved by using charcoal and activated charcoal, respectively, at pH 5, 150 rpm, 60 min of contact time, 0.5 g of adsorbent dosage, and 0.1 mg/L of Cr (VI) initial concentration. The removal of Cr (VI) was mainly affected by adsorption operating conditions and the physicochemical properties of adsorbents. Langmuir and Freundlich adsorption isotherms were applied to model the adsorption behaviour and determine the adsorption capacity of both PET charcoal adsorbents. The adsorption isotherm plot was well fitted with the Langmuir model.

1. Introduction

Heavy metals, which have the potential to be toxic and can cause cancer in nature, are released into the water by various industries. It is posing a significant hazard to humans and aquatic habitats. Consequently, removing heavy metals from wastewater has become a major concern. Adsorption is a popular method for removing heavy metals found in wastewater due to its inexpensive, accessibility, and environmental friendliness [1]. Heavy metals are removed from wastewater using commercial adsorbents and bio-adsorbents with excellent removal capacities [1].

Plastic is a range of synthetic or semisynthetic materials that use polymers as their main ingredient. Plastic is one of the most utilized and important materials in our lives due to its low-cost production, versatility, durability, flexibility, and convenience. In Malaysia, in 2019, about 1.6 million tonnes of plastics had been brought to market, and 1.4 million tonnes of plastic waste were needed to dispose [2]. From this number, only 24 % of plastics were recycled, 13 % were either processed for energy recovery or disposed of in sanitary landfills, and the remaining 63 % were left to environment without proper disposal [2]. Inefficient plastic disposal contributes to land and water pollution since plastic is not biodegradable, and its accumulation in the environment poses a threat to the Earth [3].

Chromium (Cr) is one of the heavy metal elements commonly found in water. Chromium hexavalent [Cr (VI)] is well known for its mutagenic and carcinogenic contamination, contacts with the environment through various origins, and the development of human activities [4]. Like other heavy metals, Cr (VI) in wastewater can be removed by the adsorption method. Removing Cr with adsorption can harness an environmental issue where adsorbent media can be produced from plastic waste, thus simultaneously diminishing pollution by reducing Cr in water [5] and improving plastic waste recycling and recovery.

Polyethylene Terephthalate (PET) is the most suitable plastic waste for recycling and energy recovery. PET waste is regarded as an effective precursor in the production of activated carbon [6] and, thus, has the potential to be used as an adsorbent.

This study aims to assess the potential of charcoal and activated charcoal adsorbents derived PET plastic waste for Cr (VI) removal in aqueous solutions and to optimize the adsorption operating conditions. The investigated adsorption operating parameters were pH, contact time, agitation speed, charcoal and activated charcoal dosage, and initial Cr (VI) concentration. Lastly, adsorption isotherm models were applied to determine the interaction between the adsorbent and the adsorbates (Cr (VI)). The adsorption isotherm models used in this study were the Freundlich and Langmuir isotherms.

2. Materials and Methods

2.1. Synthesis of PET adsorbents

Plastic waste used in this study was polyethylene terephthalate (PET) plastic, which is plastic bottle. The PET plastic bottle was washed to remove dirt, cut into 2 cm x 2 cm of size, and dried at 105 °C overnight. The plastic was wrapped in aluminum foil before undergoing the pyrolysis process. The furnace was set to 450 °C, and once it reached that temperature, the wrapped plastic was put into the furnace for about 60 minutes of holding time for plastic to charcoal conversion. Some portions of PET charcoal were separated for the activation process to produce PET activated charcoal. The chemical activation used was 1M potassium hydroxide (KOH). PET charcoal was activated by immersing in 1M KOH solution for 24 hours; with the ratio was 1 g of PET charcoal to 50 mL of KOH solution. The mixture was stirred for 1 hour and left to stand for 24 hours. Upon activation, PET activated charcoal was cleaned with distilled water and dried in an oven. Both PET charcoal and PET activated charcoal produced were used as adsorbents to remove Cr (VI) in aqueous solutions.

2.2. Chemical preparation

Cr (VI) stock solution with a concentration of 1000 mg/L was prepared by mixing a known quantity of potassium dichromate ($K_2Cr_2O_7$) with 800 mL of distilled water. Once $K_2Cr_2O_7$ was dissolved completely, distilled water was added until the solution reached its final volume of 1000 mL. Stock solutions were further diluted to obtain the required Cr (VI) concentrations in solutions. Required Cr (VI) solutions were 0.1, 0.2, 0.3, 0.4, and 0.5 mg/L.

pH of the aqueous solution was adjusted with HCl to produce a solution whose pH ranged between 3 and 7. When adjusting the pH of the Cr (VI) solution, a magnetic bar was put in the solution to stir HCl and solution well thoroughly. In this study, the pH solution was chosen only in the range of 3 to 7 to avoid precipitation of insoluble chromium (III) hydroxide [$Cr(OH_3)$] in the solution [7].

2.3. Batch mode adsorption experiment

The experiments for the removal of Cr (VI) in aqueous solutions were executed in batch mode. The PET charcoal and PET activated charcoal adsorbents were inserted into 100 mL of various Cr (VI) concentrations in aqueous solution, which ranged from 0.1 to 0.5 mg/L at different pH values starting from 3 to 7 in a flask. The flask was agitated at various speeds between 0 and 200 rpm in a rotary shaker, with contact time ranging from 15 to 75 min. The conditions of the adsorption experiment are listed in Table 1. The experiment was conducted at room temperature. The final Cr (VI) concentration in an

aqueous solution was determined by *Atomic Absorption Spectroscopy (AAS)*. The one factor at a time (OFAT) method was employed to optimize the adsorption condition. Upon completing the adsorption experiments, adsorption isotherms were investigated. Langmuir and Freundlich isotherms describe the sorption or coverage of molecules on an adsorbent. Equilibrium studies are important in an adsorption system, which will be described by the isotherm. By comparison, a higher correlation coefficient between both isotherms will show and offer a better-fitting model for the adsorption process.

Table 1. Adsorption operating conditions experiment.

pH	Contact time (min)	Agitation speed (rpm)	Adsorbent dosage (g)	Initial concentration (mg/L)
3 - 7	60	100	0.1	0.5
Optimized	15 - 75	100	0.1	0.5
Optimized	Optimized	0 - 200	0.1	0.5
Optimized	Optimized	Optimized	0.1 - 0.5	0.5
Optimized	Optimized	Optimized	Optimized	0.1 - 0.5

3. Results and Discussion

3.1. Effect of adsorption conditions

3.1.1. pH

The trend of Cr (VI) removal as a function of pH solution is presented in Fig. 1. At pH 3, Cr (VI) removal is low, about 10 % for both adsorbents. At lower pH, acid CrO^{2-}_4 is dominant and ionic mobility in water, H_3O^+ is high, thus, there is only slight removal because the proton favorably competes for active sites on the adsorbent [8]. This resulted in the slow kinetics of the adsorption process [7].

As pH increases, Cr (VI) removal in solution increases remarkably until achieving an optimum pH of 5. At this point, maximum Cr (VI) removal is 42 % and 52 % for PET charcoal and PET activated charcoal, respectively. This result agreed with the finding conducted by Dehghani et al. [9]. According to Dehghani, removal is incredibly high at pH 5 due to the weakening of electrostatic force between oppositely charged PET charcoal adsorbent and CrO^{2-}_4 which results in a reduction of adsorption capacity [10].

Higher than pH 5, the removal of Cr (VI) drastically decreases due to competition between OH^- and CrO^{2-}_4. Saleh [11] denoted that lower adsorbent chemical affinity signify less tendency of CrO^{2-}_4 to interact or bind with PET charcoal and PET activated charcoal.

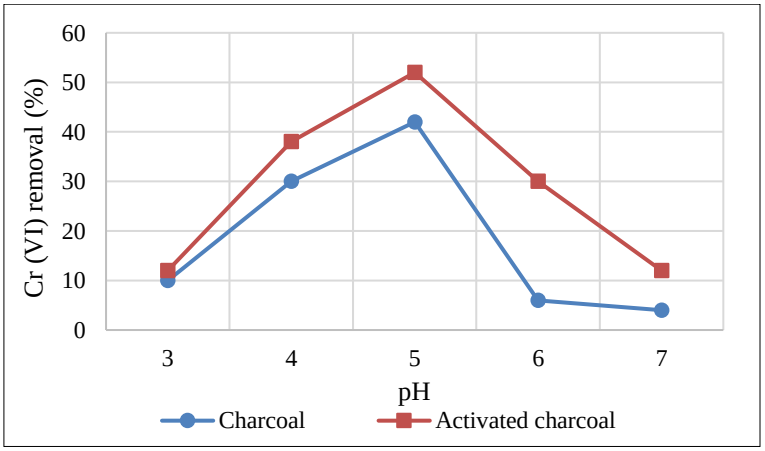

Figure 1. Cr (VI) removal versus pH.

3.1.2. Contact time

Contact time plays a major role in removal efficiency as it ensures all the available sites of adsorbent can adsorb Cr (VI). Fig. 2 shows the trend of Cr (VI) removal as contact time increased from 15 to 75 min. As shown in Fig. 2, Cr (VI) removal increased during the first 45 minutes. Adsorption is higher within the first 45 minutes since there are a lot of binding sites available for adsorption. According to Dehghani et al. [9] and Baral et al. [10], the adsorption rate was expeditious in the initial stages, then gradually flattened and became constant when equilibrium was reached [10].

At 45 minutes of contact time, the Cr (VI) removal is started to constant at 56 % for PET activated charcoal, while for PET charcoal, the Cr (VI) removal still occurred. By considering both adsorbents, the 45 minutes of sorption process is sufficient to remove Cr (VI) where the entire surface area of adsorbents have been loaded and saturated with Cr (IV). Thus, in this study, 60 minutes of contact time was chosen to ensure that adsorption equilibrium was achieved.

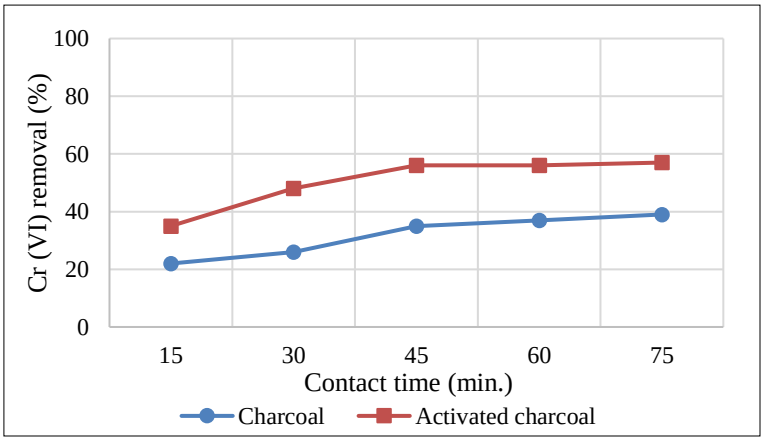

Figure 2. Cr (VI) removal versus contact time.

3.1.3. Agitation speed

The contact between the adsorbent and the adsorbate is affected by the agitation speed. Agitation facilitates proper contact and effective transfer between CrO^{2-}_4 and adsorbent binding sites [12]. The pattern of Cr (VI) removal due to agitation speed is presented in Fig. 3. The agitation speed range from 0 to 200 rpm shows that the adsorption of Cr (VI) is rapidly increased and reaches equilibrium around 150 rpm. This effect was caused by the decrease in boundary layer thickness around adsorbent particles by increasing the degree of mixing [8].

The data in Fig. 3 shows that, at 150 rpm of agitation speed, maximum Cr (VI) removal by using PET activated charcoal is 65 %, higher than PET charcoal, 55 %. Since 150 rpm is adequate for maximum Cr (VI) removal, then 150 rpm is chosen as the optimum agitation speed. This result allied with Saifuddin [7], who chose an agitation speed of 150 rpm as the optimum speed.

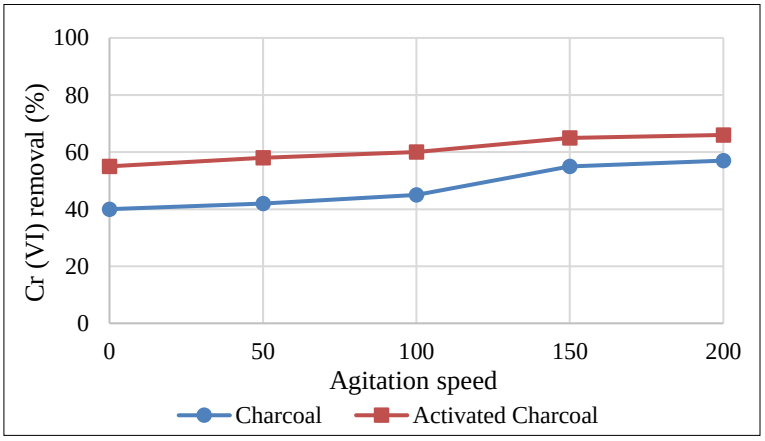

Figure 3. Cr (VI) removal versus agitation speed.

3.1.4. Adsorbent dosage

Dependency of Cr removal in relation to the amount of adsorbent dose was studied by increasing the adsorbent dosage from 0.1 to 0.5 g. The pattern of Cr (VI) removal as a function of adsorbent dosage is illustrated in Fig. 4. It can be observed that the percentage of Cr (VI) removal can be improved by increasing the adsorbent dosage. This can be expected since a higher dosage of adsorbent provides a higher surface area and greater availability of exchangeable sites for CrO^{2-}_4. Another researcher, such as Gupta et al. [8], Dehghani et al. [9] and Baral et al. [10], also showed the same pattern of adsorbate removal. All of them showed increasement when higher dosage was added (0.2 – 0.5 g).

By referring to Fig. 4, maximum Cr (VI) removal efficiency is recorded at 75 % for 0.3 g of PET activated charcoal and 71 % for 0.5 g of PET charcoal. The next addition of adsorbent dosage shows insignificant Cr (VI) removal. Study conducted by Gupta et al. [8] also showed similarity. Gupta stated that after adding the optimum dose of adsorbent, maximum adsorption is reached and the number of free ions in solution remains constant even with higher additions of adsorbent.

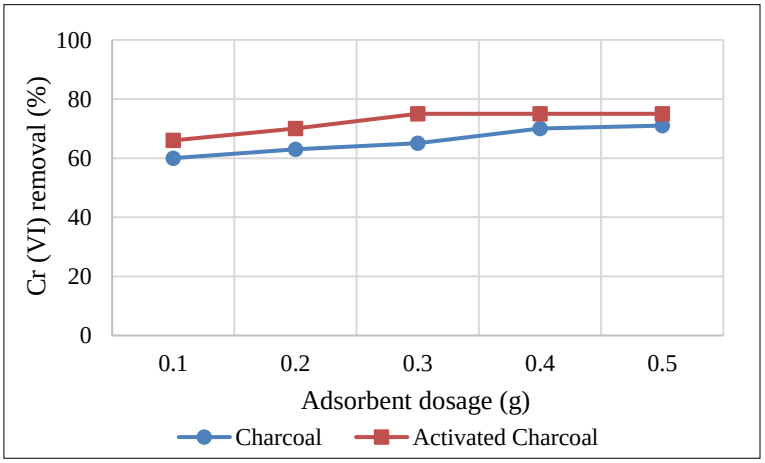

Figure 4. Cr (VI) removal versus adsorbent dosage.

3.1.5. Initial concentration

Fig. 5 shows the pattern of Cr (VI) removal with respect to the initial concentration of solution. As initial concentration increases, the Cr (VI) removal is decreased. The highest removal recorded at 0.1 mg/L at 80 % for PET charcoal and 90 % for PET activated charcoal, indicated that 0.1 mg/L is the optimum initial concentration for Cr (VI) removal. At concentrations higher than 0.1 mg/L, the adsorption capacity is decreased as a result of the active binding sites of the adsorbents being fully saturated by

CrO^{2-}_4. This result agreed with research conducted by Baral et al. [10], which also showed similarity as percentage adsorption decreased with increasing initial concentration of the adsorbate.

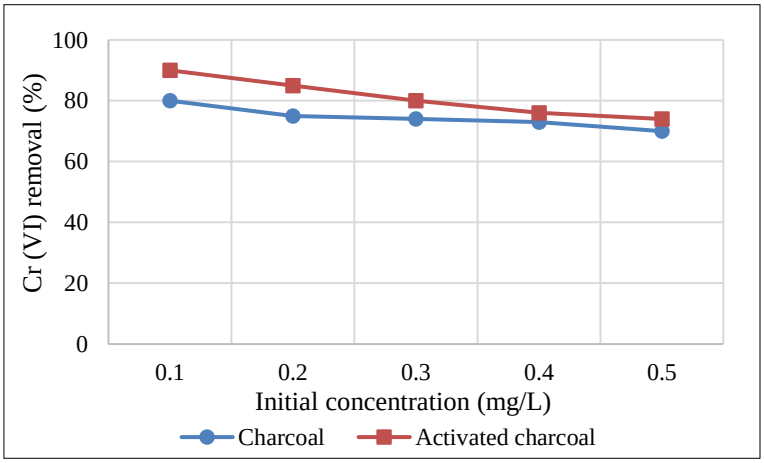

Figure 5. Cr (VI) removal versus initial concentration.

3.1.6. Summary of optimum operating parameter

Table 2 lists the optimum conditions of the adsorption process for Cr (VI) removal in aqueous solution between PET charcoal and PET activated charcoal. Based on the results presented in Figs. 1 to 5, PET activated charcoal indicates a higher removal of Cr (VI) in aqueous solutions than PET charcoal. This is due to the surface area of PET activated charcoal is recorded at 262 m^2/g, while that of PET charcoal is 66 m^2/g [13]. A larger surface area provides larger adsorption sites. In addition, activated charcoal has more enhanced pores and higher adsorption capacities than charcoal.

Table 2. Summary of adsorption optimal conditions.

Operating parameter	PET Charcoal	PET Activated charcoal
Optimum Cr (VI) removal (%)	80	90
pH	5	5
Contact time (min.)	60	45
Agitation speed (rpm)	150	150
Adsorbent dosage (g)	0.5	0.3
Initial concentration (mg/L)	0.1	0.1

3.2. Adsorption isotherm

3.2.1. Langmuir isotherm

The parameters and correlation coefficient of the Langmuir isotherm for PET charcoal and PET activated charcoal are plotted in Fig. 6. Higher correlation coefficients ($R^2 > 0.99$) show the applicability of the Langmuir model with the Cr (VI) adsorbed onto the adsorbent surface and forming a monolayer.

3.2.2. Freundlich isotherm

The Freundlich model can be applied to multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogenous surface. Fig. 7 show Freundlich model in linearized form.

3.2.3. Summary of adsorption isotherm

The summary of adsorption isotherm for PET charcoal and PET activated charcoal is listed in Table 3. Based on the linear regression values ($R^2 > 0.99$) which are considered as a measure of the goodness-of-fit of data, the experimental data follow the order, Langmuir > Freundlich.

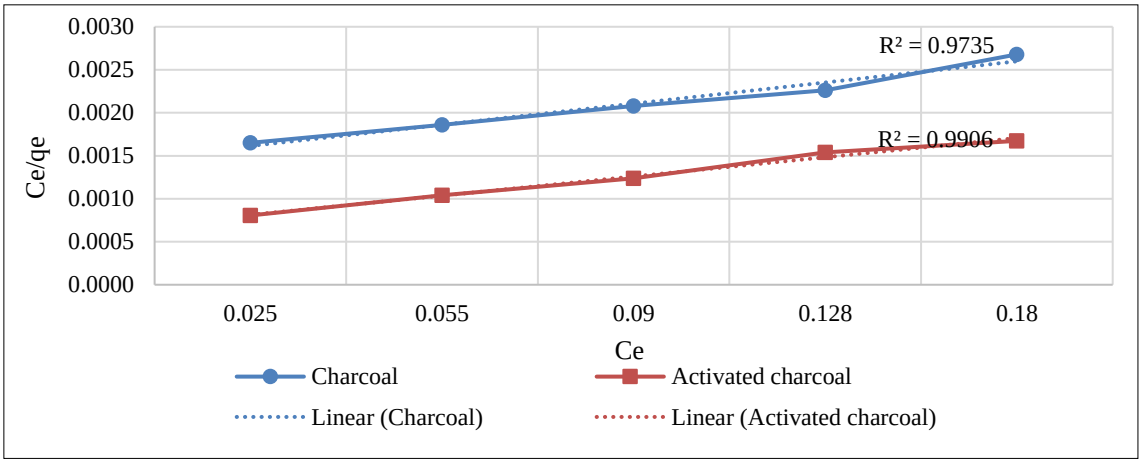

Figure 6. Langmuir isotherm model.

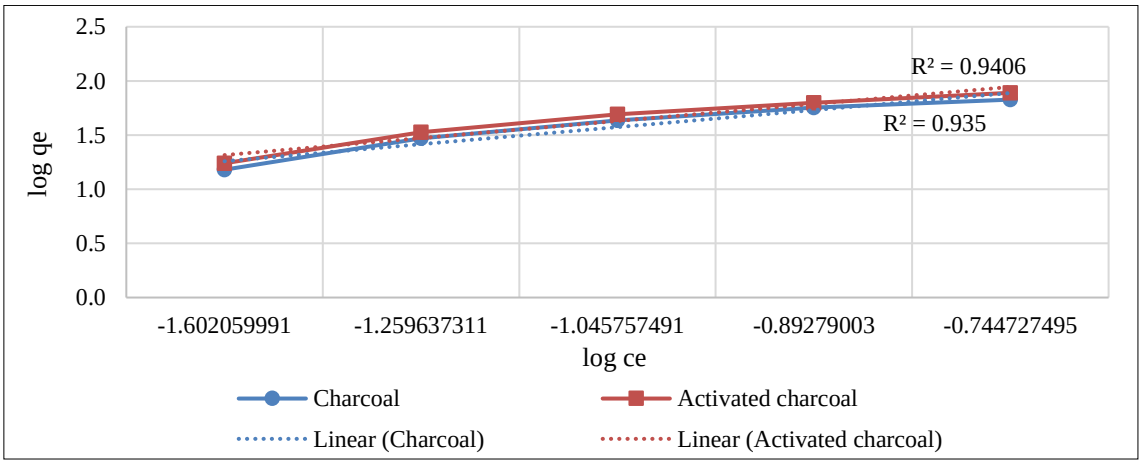

Figure 7. Freundlich isotherm model.

Table 3. Estimated linear regression values R^2 of adsorption isotherm.

Adsorbent	Langmuir isotherm	Freundlich isotherm
PET charcoal	0.9375	0.935
PET Activated charcoal	0.9906	0.9406

4. Conclusion

In this study, charcoal and activated charcoal were successfully derived from PET. The diameter of the charcoal derived PET produced was 600 µm. The first objective is to optimize the adsorption condition process for Cr (VI) removal from aqueous solution under different adsorption conditions, namely pH, contact time, agitation speed, adsorbent dosage, and solution initial concentration. The results indicated that 80 % and 90 % of Cr (VI) removal were achieved using PET charcoal and PET activated charcoal, respectively, at pH 5, 150 rpm, and 60 minutes of contact time for 0.5 mg of dosage with a 0.1 mg/L initial concentration. The removal of Cr (VI) is mainly affected by the optimal condition and

physiochemical properties of the adsorbent. Result indicates that charcoal and activated charcoal derived PET has potential as an adsorbent for Cr (VI) removal. The second objective is to model the adsorption behaviour with Langmuir and Freundlich isotherms. The adsorption isotherm plot was well fitted with the Langmuir model with $R^2 > 0.99$.

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