

Adsorption Kinetics and Thermodynamics of Lead Ions onto Chemical Activated Carbon Derived from Waste Tire Pyrolysis Char

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The pollution resulting from the generation of waste tires is currently causing adverse environmental problems worldwide. Heavy metals present in water is also a significant cause of health and environmental problems in developing countries. This study focuses on the development of activated carbon using waste tire pyrolytic char as a precursor and using the resulting activated carbon to treat water containing Pb²⁺. The results obtained from the study showed that waste tire activated carbon could effectively remove Pb²⁺ from aqueous solution far better than waste tire pyrolytic char. The effects of process variables: Temperature (°C), Contact time (min), and Initial metal concentration (mg/l) were studied and the optimum operating conditions were obtained as 25°C, 120 min, and 400mg/l for the temperature, contact time, and initial metal concentration, respectively. Adsorption kinetics revealed that the experimental data gave the best fit for the pseudo-second-order kinetic model. Adsorption thermodynamics illustrated that the adsorption process was exothermic and spontaneous in nature by calculating adsorption parameters ΔH , ΔG and ΔS as -85.57 kJ/mol.K, 4.211 kJ/mol.K, and -0.279 kJ/mol.K respectively at 298.15K.

1. Introduction

The generation of waste tires is increasing extraordinarily throughout the world with the rapid increase in automobiles. The rubber tire industry uses several raw materials that are of great importance to produce tires having specific properties for use in automobiles. Natural rubber, synthetic rubber, carbon black, and additives are the raw materials involved in manufacturing tires (Kim et al., 2017). Although the raw materials used are essential in the production of rubber tires, they also lead to some difficulties regarding the disposal of waste tires because the waste tires are non-biodegradable due to the raw materials used in the production process (Hao et al., 2001). Landfilling has been applied as a method of disposal of waste tires, but this method is currently not favoured because the waste tires occupy large spaces of landfill sites. The waste tires tend to rise to the surface of the landfill space, thus damaging the landfill cover and further causing environmental concerns.

In the past, waste tires were incinerated, which reduced their weight by 90% of their original weight. Nevertheless, the process is considered to cause some adverse environmental effects due to the release of toxic and hazardous gases such as SO₂ and NO_x. Pyrolysis, on the other hand, is seen as a more environmentally friendly method for utilizing waste tires to produce valuable products and eliminate the problems associated with disposing of waste tires. Pyrolysis involves the thermal destruction of waste tires at elevated temperatures (400 °C – 800 °C) under inert conditions whereby the long polymer chains of the waste tires are broken down into pyrolysis oil, gas, and char (Malise et al., 2020). The pyrolysis oil fraction can be used to produce fuel oil, which can be used in the combustion boilers and petroleum refineries (Choi et al., 2014). Pyrolysis gas contains carbon dioxide, methane gas, and other combustible gases, and is very calorific. The gas can find use as fuel in the pyrolysis process as a source of energy (Antoniou and Zabaniotou, 2015).

The char produced by pyrolysis of waste tires can be used for a variety of purposes, depending on its composition. Carbon black can be recovered from waste tire pyrolysis char and used as a reinforcement filler in rubber tires. It can also be used as a precursor for activated carbon production, which can be used as an adsorbent in water purification and for storing gases (Martínez et al., 2019). The use of waste tire pyrolysis char in the production of activated carbon involves an activating process that yields activated carbon with good adsorption characteristics such as large porosity, high internal surface area, and good surface chemistry (Lopez et al., 2012). Activation can be achieved through chemical activation, physical activation, or a combination of both methods (Malise et al., 2020). Physical activation involves the use of substances such as super-heated steam or CO₂ at high temperatures (Preciado-Hernandez et al., 2019), while chemical activation involves impregnation of the char with chemical reagents such as KOH, K₂CO₃, NaOH, Na₂CO₃, etc. in order to enhance the adsorption characteristics of the activated carbon product.

According to research reports, waste tire char derived activated carbon has good adsorption capabilities for use in wastewater streams containing heavy metals and as a gas storage medium. (Nieto-Márquez et al., 2017) showed that activated carbon derived from tires is highly efficient for removing trace metals Pb²⁺ and Cr³⁺ from wastewater using adsorption due to functional groups present on the surface of the activated carbon. The goal of this study was to develop activated carbon derived from waste tire pyrolytic char by chemical activation with KOH. Pb²⁺ removal efficiency from an aqueous solution was investigated as a function of several process variables. Adsorption kinetics and thermodynamics were analysed to determine the rate limiting step and understand the nature of the adsorption process.

2. Materials and Methods

2.1 Materials

The starting material for this study was waste tire pyrolysis char obtained from a local supplier. Chemical reagents used in this study were obtained from Sigma Aldrich (Pty), including KOH, NaOH, HCl, and Pb(NO₃)₂.

2.2 Adsorbent preparation

The waste tire char was first washed in distilled water and then dried at 100°C for 24 hours in a drying oven. The dry waste tire pyrolysis char was then sieved to the required sieve size of 100µm. The sieved sample was impregnated with an aqueous solution of KOH at an impregnation ratio of 2:1 (g of KOH/g of waste tire pyrolysis char). The mixture was placed on a stirrer for 200 rpm and 80°C for 24 hours to facilitate the impregnation process. After stirring, the slurry mixture was dried at 100°C in a drying oven for 24 hours, and the dry sample was later taken to a tube furnace operating at a temperature of 600°C for 1 hour under nitrogen atmosphere to carry out the activation step further. Activated carbon samples were washed in 1M HCl to remove ash and Sulphur, content and then dried overnight.

2.3 Adsorbent experiments

A series of experiments was conducted to determine the effect of process variables contact time, temperature, and initial metal concentration on the adsorption of Pb²⁺ from an aqueous solution. The adsorption experiments were carried out using both waste tire pyrolysis char and waste tire activated carbon to determine the percentage removal of Pb²⁺ from an aqueous solution. The experiments took place in a shaking incubator operating at a stirring speed of 200rpm using 100ml Erlenmeyer flasks as containers for the samples during the adsorption process. After the adsorption process, the samples were quickly filtered using 125µm filter paper, and the filtrate solutions were analysed using an atomic absorption spectrometer (AAS). Eq. 1 below shows the determination % removal of Pb²⁺.

$$\% \text{ removal of } Pb^{2+} = \frac{C_i - C_o}{C_i} \times 100 \quad (1)$$

Where C_i is the initial concentration of the Pb²⁺ initially present in solution before the adsorption process and C_o is the concentration of Pb²⁺ after the adsorption process.

2.4 Adsorption kinetic models

Adsorption kinetics were applied in this study to determine the rate controlling step for the adsorption process. The adsorption kinetics models applied in this study include Lagergren's pseudo-first-order, Ho's pseudo-second-order, and intraparticle diffusion kinetic models. Lagergren's pseudo-first-order kinetic model is considered one of the earliest kinetic models used to describe the adsorption of solids in solid-liquid systems. The pseudo-first-order kinetic model is expressed by Eq. 2:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

Where q_e and q_t are the concentrations of the metal ions adsorbed at equilibrium and time t (mg/g), respectively. K_1 is the pseudo-first-order rate constant of the reaction (min^{-1}).

Ho's pseudo-second-order kinetic model in Fig. 3(B) advises that chemisorption, which involves violent forces comprised of the sharing of electrons between the adsorbent and the adsorbate, is the rate-limiting step controlling the process. Ho's pseudo-second-order kinetic model is described by Eq. 3

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

Where q_t and q_e are the concentration of the lead ions adsorbed after time t (min) and at equilibrium, respectively and k_2 is the pseudo-second-order reaction rate constant.

Intraparticle diffusion kinetic model introduced by Weber and Morris has been widely applied to determine the rate-limiting step in the adsorption of heavy metals and Eq. (4) is used to describe the intraparticle diffusion kinetic model.

$$q_t = k_i t^{1/2} + C \quad (4)$$

Where q_t (mg/g) is the concentration of lead ions adsorbed after time t (min) has been reached, k_i is the intraparticle diffusion rate constant, and C is the intercept. A plot of q_t vs $t^{1/2}$ must be a straight line passing through the origin, with k_i being the slope of the plot for intraparticle diffusion to be the primary rate-limiting step.

2.5 Adsorption Thermodynamics

Adsorption thermodynamics were evaluated in this study to determine whether the adsorption of lead ions onto waste tire activated carbon and waste tire pyrolysis char is a spontaneous process in nature or not. Thermodynamic parameters such as the enthalpy change (ΔH°), Gibbs free energy change (ΔG°), and entropy change (ΔS°) were determined. Eq. (5), Eq. (6) and Eq. (7) were used to determine the values of these adsorption thermodynamics parameters.

$$\Delta G = -RT \ln K_D \quad (5)$$

$$\ln K_D = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (6)$$

$$K_D = \frac{q_e}{C_e} \quad (7)$$

Where ΔG is the Gibbs free energy change (kJ/mol), R is the universal gas constant (8.314 J/mol.K), T is the absolute temperature of the solution (K), K_D is the distribution coefficient or equilibrium constant dependent on temperature, ΔH° is enthalpy change (kJ/mol.K), ΔS° is entropy of the process (kJ/mol.K).

3. Results And Discussions

3.1 Adsorption studies

3.1.1 Effect of contact time on the % removal of Pb^{2+} from aqueous solution using WTAC and WTPC

The effect of contact time on the percentage removal of Pb^{2+} is shown in Figure 1(A). The percentage removal of Pb^{2+} increased as the contact time increased for both the waste tire activated carbon and the waste tire pyrolysis char. The notable observation was that WTPC and WTAC reached equilibrium at 120 min. It is also important to note that the percentage removal of Pb^{2+} by WTAC was higher than WTPC. At 120 min, the % removal WTPC and WTAC were 41 and 91%, respectively. For WTPC and WTAC, there was a rapid increase in the percentage removal of Pb^{2+} at a contact time of between 40-100 min because adsorption takes place rapidly in the early stages due to the presence of adsorption sites on the surface of the WTPC and WTAC. Beyond 120 min, the percentage removal of Pb^{2+} reduces very slightly because WTPC and WTAC have limited adsorption sites. In other words, the saturated point reaches and no more adsorption of the Pb^{2+} onto active sites takes place. As a result, 120 min was chosen as the optimum contact time for both WTPC and WTAC.

3.1.2 Effect of initial metal concentration on the % removal of Pb^{2+} from aqueous solution using WTAC and WTPC

The effect of initial metal concentration on the % removal of Pb^{2+} by WTPC and WTAC is depicted in Figure 1(B). As shown in Figure 1(B), WTAC achieved higher % removal of lead ions than WTPC due to the chemical activation that took place. For both WTPC and WTAC, as the initial metal concentration increased, the % removal of lead ions increased until an initial metal concentration of 400mg/l. The % removal of the lead ions decreased gradually as the metal concentration was increased above 400 mg/l. The increase in the % removal of lead ions resulting from an increase in the initial metal concentration is due to the increased concentration gradient between the bulk lead ions in solution and the availability of adsorption sites on the surface of the WTPC and WTAC (Tan et al., 2016). Therefore, an initial metal concentration of 400mg/l is considered the optimum initial metal concentration in this study.

3.1.3 Effect of temperature on the % removal of Pb²⁺ from aqueous solution using

Figure 1(C) depicts the effect of temperature on the % removal of lead ions for both WTAC and WTPC. An increase in temperature from 25°C to 50°C resulted in a decrease in the % removal of lead ions from 92% to 40% for WTAC and 37% to 11% for WTPC. This behaviour suggests that the adsorption of lead ions onto WTPC and WTAC is an exothermic process. The decrease in the percentage removal of lead ions as the temperature is due to the weakening of the attractive forces between the adsorption sites on the surface of the adsorbent and the lead ions in solution as the temperature increases.

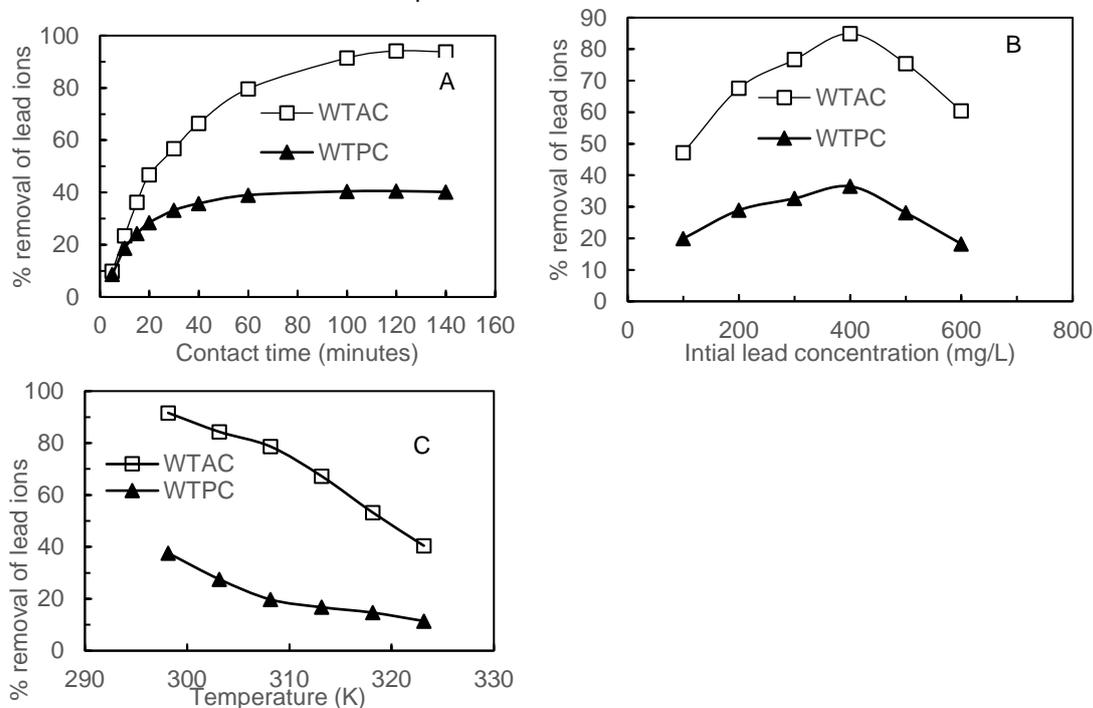


Figure 1: Effect of contact time (A), Initial lead concentration (B) and temperature (C) on the % removal of lead ions from aqueous solution using Waste tire activated carbon (WTAC) and waste tire pyrolysis char (WTPC) (The adsorbent dosage, pH, contact time and temperature were kept constant at 0.25 g/100 ml, 7, 120 min and 25°C respectively).

3.2 Adsorption kinetics

Figure 3(A) shows the pseudo-first-order kinetic model constants for the adsorption of lead ions onto WTAC and WTPC. The plots in Figure (3A), were used to determine the values of k_1 . The rate constants obtained were 0.0425 min^{-1} and 0.0357 min^{-1} for WTAC and WTPC, respectively. It can be seen from Table 4 that the pseudo-first order kinetic model obtained the highest correlation coefficients for the adsorption of lead ions onto WTAC and WTPC as $R^2 = 0.9981$ and $R^2 = 0.9762$, respectively. The value of k_2 was calculated from the plot of t/q_t as $0.00389 \text{ (g/mg.min)}$ and $0.00039 \text{ (g/mg.min)}$ for the adsorption of lead ions onto WTAC and WTPC, respectively. The correlation coefficients for the pseudo-second-order kinetic model were higher than those for the pseudo-first-order kinetic model, which suggests that the process is controlled by chemical adsorption. As shown in Figure 3(C) illustrates that q_t vs $t^{1/2}$ did not pass through the origin, suggesting that intraparticle diffusion is not the rate-limiting step. Still, the adsorption kinetics may be controlled by film diffusion in the initial stage of the reaction, followed by intraparticle diffusion later. The correlation coefficients obtained for the intraparticle diffusion kinetic model were 0.929 and 0.897 for the adsorption of lead ions onto WTAC and WTPC, respectively. Both the correlation coefficients were lower than both the pseudo-first-order and second-order kinetic models. Since the plot of qt vs $t^{1/2}$ does not go through the origin, this suggests that intraparticle diffusion is not the sole rate-limiting step, but it might be accompanied by film diffusion.

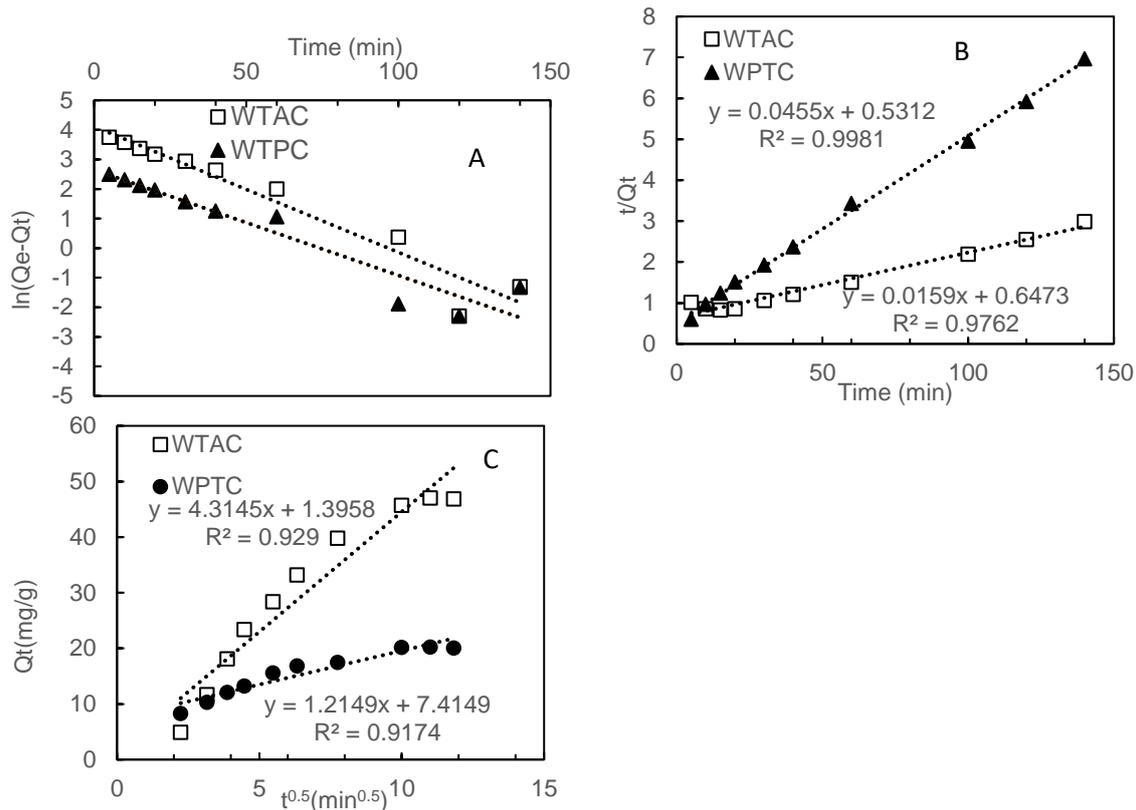


Figure 3: Lagergren's pseudo-first-order (A), Ho's pseudo-second-order (B) and Weber and Morris intraparticle (C) kinetic model plot for the adsorption of lead ions onto WTAC and WTPC

Table 4: Adsorption kinetics constant for the adsorption of lead ions onto WTAC and WTPC.

	Pseudo 1 st order kinetic		Pseudo 2 nd order		Intraparticle diffusion		
	K_1 (min ⁻¹)	R^2	K_2 (g/mg.min)	R^2	K_i (mg/g.min ^{1/2})	C	R^2
WTAC	0.0425	0.9386	0.00389	0.9981	4.3145	1.395	0.929
WTPC	0.057	0.9097	0.00039	0.9762	1.2149	7.415	0.897

3.3 Adsorption thermodynamics

Table 5: Thermodynamic parameters for the adsorption of lead ions onto WTPC and WTAC.

Temperature (K)	ΔG° (kJ/mol.K)	ΔG° (kJ/mol.K)	ΔH° (kJ/mol.K)	ΔH° (kJ/mol.K)	ΔS° (kJ/mol.K)	ΔS° (kJ/mol.K)
	WTPC	WTAC	WTPC	WTAC	WTPC	WTAC
298.15	-2.972	4.211	-47.27	-87.57	-0.169	-0.279
303.15	-4.186	2.493				
308.15	-5.371	1.566				
313.15	-5.981	0.069				
318.15	-6.491	-1.490				
323.15	-7.363	-2.901				

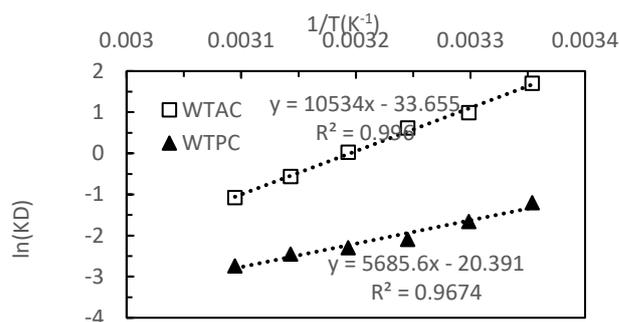


Figure 4: Plot of $\ln K_D$ vs $1/T$ for the estimation of adsorption thermodynamic parameters for the adsorption of lead ions onto WTPC and WTAC.

4. Conclusion

The effect of different process parameters (contact time, initial metal concentration and temperature) on % removal of lead ions using WTPC and WTAC were determined and optimised. A high lead ions removal efficiency was obtained at process conditions (initial concentration of 400mg/l, contact time of 120 min and a temperature of 25°C). Adsorption kinetics showed that chemisorption is the rate-limiting step for the process as the Pseudo second-order kinetic model provided the best fit. Thermodynamic parameters from this study suggest that the process is exothermic in nature and spontaneous at lower temperatures. The thermodynamic parameters also showed decreased randomness at the solid/liquid interface during the adsorption of lead ions onto waste tire activated carbon.

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