

Adsorption of Lead Ions onto Chemical Activated Carbon Derived From Waste Tire Pyrolysis Char: Equilibrium and Kinetics Studies

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The environmental impacts caused by the disposal of waste tires on land and impacts of metals in water is of great concern. In this study activated carbon was prepared from waste tire pyrolysis char using a chemical activation process where KOH was used as an activating agent at 600 °C in a tube furnace. The characterization techniques namely proximate analysis and X-ray fluorescence (XRF) were used. The adsorption results revealed that waste tire activated carbon (WTAC) was more effective than waste tire pyrolysis char (WTPC) on the removal of lead ions from aqueous solution. The effect of adsorption process parameters such as: adsorbent dosage and pH on adsorption of lead ions onto WTPC and WTAC were determined and optimized. A high lead ions removal efficiency was obtained at following process conditions namely: pH of 7 and adsorbent dosage of 0.25g/100ml. Adsorption isotherms studies revealed that the experimental data was best fitted with Freundlich isotherm model. The proximate analysis and XRF analysis confirmed that chemical activation of waste tire pyrolysis char took place.

Keywords: Waste tire activated carbon, Adsorption, Adsorption isotherms

1. Introduction

Heavy metals pollution in water has remained a critical concern throughout the world for many years, more especially in developing countries due to industrial activities (Bagbi et al., 2016). The major concern with heavy metals is that they are very toxic and non-biodegradable hence a health hazard to humans and animal life (Mousavi et al., 2010). The most dangerous heavy metals to human health include Cu, Zn, Cd, Fe, Hg, Mn, and Pb ions. Amongst all these heavy metals, Pb²⁺ ions are one of the most hazardous posing serious health threats due to its presence in most wastewater streams (Momčilović et al., 2011). Pb²⁺ is mostly introduced into the environment through industries such as battery manufacturing companies, mining companies, pigments and paints manufacturers, and explosives manufacturing companies (Dil et al., 2017). According to the World Health Organization (WHO), the tolerance limit for Pb²⁺ ions concentration in drinking water should not exceed 0.05 mg/l (Asuquo et al., 2017). Exposure to Pb²⁺ at concentrations above the acceptable limit can lead to severe health problems to humans and this effects include kidney problems, fertility problems, brain and liver damage, and problems in the nervous system (Asuquo et al., 2017).

Several techniques have been applied to remove Pb²⁺ ions from wastewater and these techniques include methods such as metal precipitation, ion exchange, membrane filtration, reverse osmosis, and adsorption (Wang et al., 2016). Amongst all these processes, adsorption of Pb²⁺ using activated carbon is gaining a lot of recognition due to its high efficiency, easy operation, low costs, and energy efficiency. Commercial activated carbon is the most used adsorbent for the adsorption of heavy metals due to its porosity, has high surface area (500 – 5000 m²/g), and has high adsorption capacities for Pb²⁺ which enables it to be suitable for the removal of Pb²⁺ (Asuquo et al., 2017). The major concern about commercial activated carbon is that it is very expensive and for this reason it's use is limited. This has led to a growing demand to produce low cost

activated carbon for the removal of Pb^{2+} ions from wastewater. Efforts have been made to produce activated carbon from agricultural wastes, solid wastes, and by-products from other processes. For example desiccated coconut waste (Rahim et al., 2019). Waste tires are creating a great environmental problem throughout the world since the rate at which they are being produced continues to increase rapidly every year and it is becoming difficult to dispose them in an environmentally friendly manner. The strict regulations restricting the disposal of waste tires into landfill sites means that there is a need for other alternative environmentally safe ways of disposing waste tires (González et al., 2006). Pyrolysis of the waste tires has been regarded as the most promising method for the utilization of the waste tires since the process can reduce the weight of the waste tires by up to 90 % of its original weight and it results in the production of by products such as waste tire pyrolysis oil, pyrolysis char and pyrolysis gas (Acosta et al., 2016).

The waste tire pyrolysis char can further be processed by activation to produce activated carbon with good adsorption properties. The activation methods include chemical and physical activation. Chemical activation involves the use of chemical reagents to produce activated carbon with superior adsorption properties (Pradhan and Sandle, 1999) and physical activation involves the use of oxidizing agents such as carbon dioxide and superheated steam to produce activated carbon with good adsorption properties (Antoniou et al., 2014). The aim of this study is to produce activated carbon from WTPC through a chemical activation process using KOH as an activating agent. Different characterization techniques were applied to investigate the physical and chemical properties of activated carbon produced. Adsorption experiments were performed to determine the effect of process variables on the percentage removal of lead ions from aqueous solution. The adsorption isotherms were used to determine the adsorption equilibrium of the adsorption process.

2. Materials And Methods

2.1 Materials

Waste tire pyrolysis char was obtained in powder form from a local company. Potassium hydroxide, sodium hydroxide hydrochloric acid and lead nitrate were of analytical grade and were obtained from Sigma Aldrich (Pty).

2.2 Adsorbent preparation

100g of waste tyre pyrolysis char (WTPC) was firstly washed with distilled water to remove impurities. The washed sample was then placed in a drying oven for 24 hours at 100°C to dry. Thereafter the sample was then sieved to a particle size less than 100µm. After sieving, the sample was impregnated with a 500ml aqueous solution of KOH at an impregnation ratio of 2:1 (weight of KOH: weight of char) and the mixture was stirred at 80°C for 24 hours to complete the impregnation process. The slurry produced from the impregnation process was dried in a drying oven at 100°C for 24 hours to remove moisture. The dry sample was activated in a tube furnace at a temperature of 600°C for 1 hour using nitrogen. After the activation the sample was washed with 1M solution of HCl to remove ash and sulphate ions and thereafter dried overnight.

2.3 Adsorbent characterization.

2.3.1 Proximate analysis

Proximate analysis was used to determine the moisture content, volatile matter, and ash content. In proximate analysis mass loss was determined by mass loss at 150 °C, the volatile matter was determined on the dried sample under nitrogen at 450 °C, the ash content determined as the mass loss at 650 °C and lastly the fixed carbon was calculated by subtracting the sum of the above from 100.

2.3.2 X-Ray Fluorescence (XRF) analysis

XRF analysis was performed to determine the elemental analysis of the sample.

2.4 Adsorbent experiments

The adsorption experiments were carried out to determine the effect of process variables namely: pH, and adsorbent dosage on the percentage removal of Pb^{2+} from aqueous solution using the waste tire activated carbon (WTAC) and waste tire pyrolysis char (WTPC) The experiments were carried out in sealed Erlenmeyer flasks and stirred in a shaking incubator operating at 200rpm. After the adsorption process the samples were filtered using 125µm filter papers. The filtrates were then diluted for analysis and analysed using an atomic absorption spectrometer (AAS) to determine the concentration of lead ions present in solution after adsorption process. The percentage removal of Pb^{2+} from aqueous solution was determined using Eq. (1).

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

Where C_i is the initial concentration of the Pb^{2+} initially present in solution before the adsorption process and C_o is the concentration of Pb^{2+} after the adsorption process.

3. Results And Discussions

3.1 Adsorbent characterization

3.1.1. Proximate analysis

Table 1 shows the results obtained from the proximate analysis. From Table 1 there was a slight increase in the moisture content and fixed carbon content and slight decrease in the volatile and ash content after WTPC was chemical activation with KOH at 600 °C. The increase in the moisture content of the WTAC has been reported in a previous study and can be attributed to an increase in the surface area of the activated carbon after the activation of the WTPC (Nieto-Márquez et al., 2016). The decrease in the volatile matter and increase in the fixed carbon content can be linked to the effect of KOH during the activation process. As the volatile matter was decreased, the fixed carbon content was increased. There was also a slight decrease in the ash content was due to the leaching process when the activated was washed with HCl.

Table 1: Proximate analysis of the raw WTPC and WTAC

| Test description (%) | WTPC | WTAC |
|----------------------|------|------|
| Moisture | 3 | 3.4 |
| Volatiles | 1.1 | 0.8 |
| Ash content | 15.3 | 12 |
| Fixed carbon | 80.6 | 83.6 |

3.1.2 X- ray fluorescence (XRF) results

Table 2 shows the results obtained from the XRF analysis. From Table 2, there was a decrease in the amount of the metals which were originally present in the char. The decrease in the amounts of the metals can be linked to the leaching effect of HCl towards the metals during the washing process after chemical activation. The increase in the amount of Potassium (K) was due to the introduction of KOH in the activation stage. (López et al., 2013) reported comparable results using acid demineralization of the char before activation. It was also observed that the inorganic matter decreased drastically after the acid demineralization of the tire pyrolysis char.

Table 2: XRF results showing the inorganic components found in WTPC and WTAC.

| Metal | WTPC (mg/kg) | WTPC (%) | WTAC (mg/kg) | WTAC (%) |
|-------|--------------|----------|--------------|----------|
| K | 76 | 1.24 | 516 | 9.82 |
| Ca | 306 | 5.00 | 215 | 4.09 |
| Ti | 17 | 0.28 | 15 | 0.29 |
| Cr | 3.1 | 0.05 | 2.06 | 0.04 |
| Mn | 4.5 | 0.07 | 4.1 | 0.08 |
| Fe | 711 | 11.62 | 631 | 12.00 |
| Co | 287 | 4.69 | 239 | 4.55 |
| Ni | 31 | 0.51 | < 0 | 0 |
| Cu | 305 | 4.99 | 261 | 4.91 |
| Zn | 4377 | 71.55 | 3374 | 64.18 |
| Total | 6117.6 | 100 | 5257.16 | 100 |

3.2 Adsorption studies

3.2.1 Effect of pH on the % removal of Pb²⁺ from aqueous solution using WTAC and WTPC.

The pH value of the solution in an adsorption plays a role in the ionization of the functional groups responsible for adsorption which are present on the surface of an adsorbent and the charge of the metal ions adsorbed. Fig. 1(A), shows the effect of pH on the adsorption of lead ions onto the surface of WTPC and WTAC. It is visible that WTAC achieved higher percentage removal of lead ions than WTPC, this shows that the chemical activation of the waste tire char produced waste tire activated carbon and this played a significant role in enhancing the adsorption properties. Fig. 1(B) also shows that as the pH value of the solution increases, the percentage removal of lead also increases until the highest removal is achieved at pH 7 from which then the percentage removal starts to decrease for both WTPC and WTAC. The high removal percentages of lead ions at low pH values takes place due to the presence of hydrogen atoms in solution at low pH values which compete with the lead ions for adsorption sites on the surface of the adsorbent. As the pH value of the solution is increased, there is an observed increase in the percentage removal of lead ions until the highest removal is

achieved at pH 7. As the pH increases beyond pH 7 the removal percentage of lead decreased. This is because as the pH of the solution increases the lead ions present in solution start to hydrolyse and as a result they cannot be removed from solution.

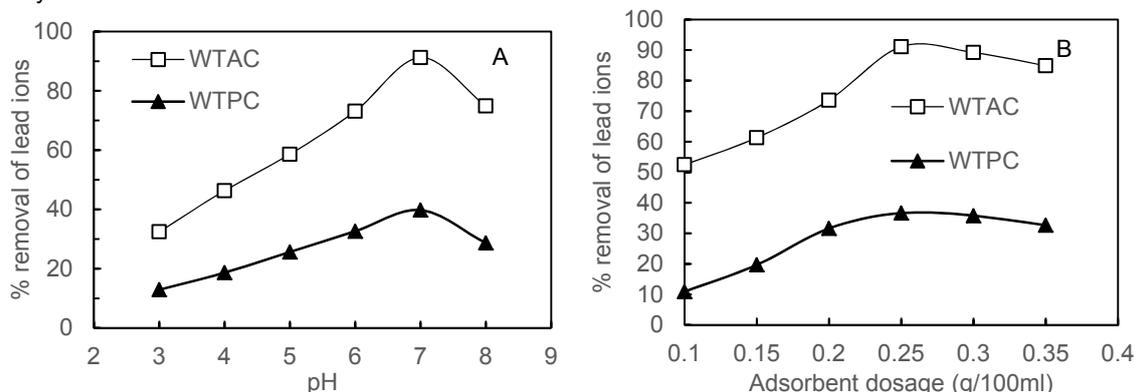


Figure 1: pH (A) and Adsorbent dosage (B) on the % removal of lead ions from aqueous solution using WTAC and WTPC (The adsorbent dosage, pH, contact time and temperature were kept constant at 0.25 g/100 ml, 7, 120 min and 25°C respectively).

3.3 Effect of adsorbent dosage on the % removal of Pb²⁺ from aqueous solution using WTAC and WTPC.

The dosage of adsorbent is one of the process variables which affect the adsorption process at a greater extent. Fig. 1(B), shows the effect of adsorbent dosage on the percentage removal of lead ions from aqueous solution. From Fig. 1(B), it is can be seen that the percentage removal of lead ions increases gradually with an increase in the adsorbent dosage from 0.1 g/100ml to 0.25g/100ml and thereafter the removal percentage remains unchanged with an increase in the adsorbent dosage from 0.25g/100ml to 0.35g/100ml for both WTPC and WTAC. The increase in the percentage removal of lead ions as the adsorbent dosage is increased from 0.1g/100ml to 0.25g/100ml is due to the availability of adsorption sites on the surface of the adsorbent leading to more lead ions being adsorbed onto the adsorption sites of the adsorbent. However, increasing the adsorbent dosage from an adsorbent dosage beyond 0.25g/100ml does not result in any further increase in the percentage removal of lead ions from aqueous solution. This behaviour takes place because at an adsorbent dosage of 0.25g/100ml an equilibrium between the adsorption sites on the surface of the adsorbent and the lead ions in solution has been reached and at this point the rate of adsorption is equal to the rate of desorption which does not affect the adsorption process. For this study, an adsorbent dosage of 0.25g/100ml was the optimum adsorbent dosage.

4. Adsorption isotherms models

Adsorption isotherms are very important in adsorption studies because they provide the necessary information relating the relationship between the amount of metal ions adsorbed onto the adsorbent at equilibrium and the concentration of the metal ions in solution at equilibrium at a given temperature (Patnukao et al., 2008). They are also important in determining the adsorption capacity of the adsorbent. In this study two adsorption isotherm models were used to describe the experimental data more accurately namely the Langmuir and Freundlich isotherm. The Langmuir isotherm model assumes monolayer coverage of the adsorbent onto the surface of the adsorbent and that adsorption only takes place at certain specific homogeneous sites on the surface of the adsorbent (Sari et al., 2007). The Langmuir isotherm model is represented by Eq. (2):

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{q_m K_L}\right) \frac{1}{C_e} \quad (2)$$

Where q_e and C_e are the concentration of the lead ions adsorbed at equilibrium (mg/g) and the concentration of the lead ions left in solution after equilibrium has been reached (mg/l). q_m is the maximum monolayer adsorption capacity (mg/g) and K_L is the Langmuir isotherm constant related to the free energy of the adsorption process (L/mg). For Langmuir isotherm model, it is important to determine a dimensionless equilibrium parameter known as the separation factor (R_L) which determines whether Langmuir isotherm model is favourable or not for the adsorption of lead ions onto WTAC and WTPC. R_L is given by Eq. (3).

$$R_L = \frac{1}{1 + K_L q_m} \quad (3)$$

A value of $R_L > 1$ implies that the model is unfavourable, $0 < R < 1$ the model is favourable, $R = 1$ the model is linear, and $R = 0$ the model is irreversible (Foo and Hameed, 2010). The Freundlich isotherm model is an empirical isotherm model used to describe adsorption processes in which adsorption takes place on the heterogeneous surface of the adsorbent and adsorption is not limited to monolayer coverage of the adsorbate on the surface of the adsorbent. The Freundlich isotherm model can be represented by Eq. (4).

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

Where q_e and C_e are the concentrations of the lead ions adsorbed at equilibrium (mg/g) and the concentration of the lead ions left in solution at equilibrium (mg/l). K_f is the Freundlich isotherm constant related adsorption capacity and $1/n$ is an empirical parameter related to the intensity of the adsorption process. A value of $1/n$ less than 1 implies that the adsorption process is favourable and a value of $1/n$ greater than 1 implies that the adsorption process is not favourable.

Table 3: Langmuir and Freundlich isotherm constants for the adsorption of lead ions onto WTPC and WTAC.

| | Langmuir | | | Freundlich | | | |
|------|--------------|---------------|-------|------------|-------|--------|--------|
| | Q_m (mg/g) | K_L (L/min) | R^2 | R_L | K_f | $1/n$ | R^2 |
| WTPC | 23.42 | 0.198 | 0.915 | 0.177 | 2.408 | 0.1792 | 0.9410 |
| WTAC | 85.91 | 0.060 | 0.908 | 0.162 | 2.356 | 0.5273 | 0.9561 |

The equilibrium data was fitted into the different adsorption isotherm models to determine which model had the best fit. Fig. 2 (A) and (B), shows the Freundlich and Langmuir isotherm plots for the adsorption of lead ions onto WTPC and WTAC respectively. Table 3 shows the isotherm constants obtained for the two adsorption models, the Freundlich isotherm model showed best fit for the experimental data achieving correlation coefficients 0.941 and 0.956 for the adsorption of lead ions onto WTPC and WTAC respectively. This implies that the adsorption of lead ions onto WTPC and WTAC is not restricted to monolayer coverage of the adsorbent onto the surface of the adsorbate and that the interaction between the adsorbents and the lead ions allows the formation of multilayers. The values of K_f and $1/n$ were calculated from the slope and intercept from Fig. 2(B). The values of $1/n$ were found to be 0.1792 and 0.5273 for the adsorption of lead ions onto WTPC and WTAC and this indicates that the adsorption process was favourable under the studied conditions (Tan et al., 2007). The correlation coefficients achieved for Langmuir isotherm model were 0.915 and 0.908 for WTPC and WTAC respectively and both these values were lower than those achieved from the Freundlich isotherm model. The maximum Langmuir adsorption capacity (q_m) and energy of adsorption (K_L) were calculated from Fig. 2(A), as 85.91 mg/g and 23.42 mg/g and 0.06 L/mg and 0.198 L/mg for WTAC and WTPC respectively. The increase in the monolayer maximum Langmuir adsorption capacity from 23.42 mg/g (WTPC) to 85.91 mg/g (WTAC) shows that the activation process plays a significant role in improving the adsorptive properties of the WTPC which results in increased adsorption capacity. The Langmuir separation factor was calculated to be 0.177 and 0.162 for WTPC and WTAC respectively and this shows that the model was favourable for the adsorption of lead ions onto WTAC and WTPC.

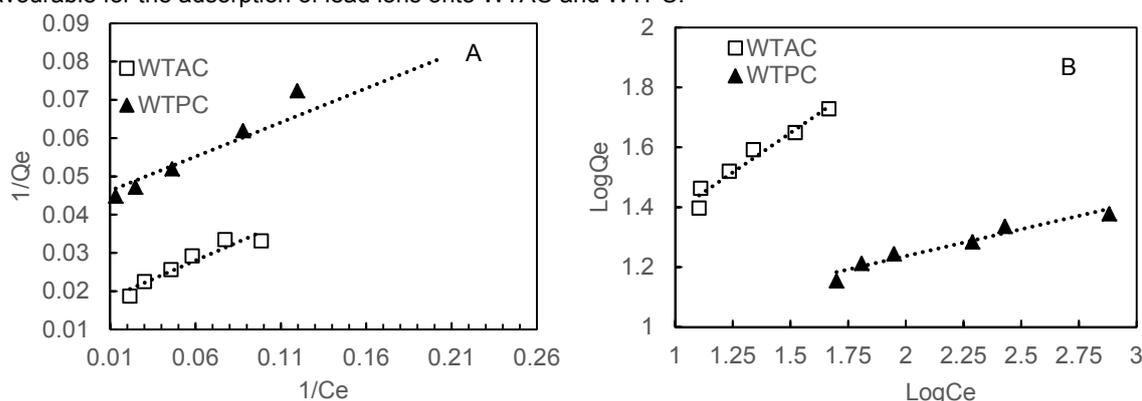


Figure 2: Langmuir (A) and Freundlich (B) isotherm plot for adsorption of lead ions onto WTAC and WTPC.

5. Conclusion

Activated carbon was prepared from waste tire pyrolysis char using a chemical activation process where KOH was used as an activating agent at 600 °C in a tube furnace. The characterization techniques namely proximate analysis and X-ray fluorescence (XRF) were used. The proximate analysis performed on the activated carbon showed a decrease in the volatile and ash content of the activated carbon produced

compared to the waste tire char. XRF analysis further confirmed that activating the waste tire char with KOH produces an activated carbon with decreased amounts of inorganic matter.

The effect of adsorption process parameter such as: adsorbent dosage and pH on the adsorption of lead ions onto WTPC and WTAC were determined and optimized. A high lead ions removal efficiency was obtained at the following process conditions namely: pH of 7 and adsorbent dosage of 0.25g/100ml. Adsorption isotherm models Langmuir and Freundlich were studied and the equilibrium data was best fitted by the Freundlich isotherm model implying that the adsorption of lead ions is not restricted to monolayer coverage of the adsorbate onto the surface of the adsorbent but instead multilayer coverage of the lead ions onto the surface of WTAC and WTPC.

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