Adsorption of Lead ions onto Activated Carbon derived from Sugarcane bagasse

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Abstract. In this study, activated carbon was developed from sugarcane bagasse and its effectiveness in adsorbing lead (Pb^{2+}) ions from synthetic aqueous solution was examined. Sugarcane bagasse activated carbon (SCBA) was developed in a tube furnace at a temperature of 900 ℃, a heating rate of 10 ℃/min, residence time of 3 hours, and at a nitrogen flow rate of 100 mL/min. Batch adsorption experiments were carried out to investigate the effects of pH and SCBA dosages on the adsorption process. The batch adsorption test showed that extent of Pb^{2+} adsorption by SCBA was dependent upon pH and SCBA dosage. The optimum pH for Pb^{2+} adsorption was found to be at pH 5.0. Maximum Pb^{2+} removal efficiency obtained from the batch studies was 87.3 % at SCBA dosage of 10 g/L. Equilibrium adsorption data was described by Langmuir model with a coefficient of determination (R^2) of 0.9508. Maximum adsorption capacity according to Langmuir model was evaluated to be 23.4 mg/g. The adsorption capacity of the SCBA was compared with that of other plant-based adsorbents. SCBA is an effective adsorbent for the removal of Pb^{2+} from aqueous solution.

1. Introduction

Wastewater containing heavy metals is increasingly release into the environment directly or indirectly, particularly in developing countries [1]. Unlike other contaminants found in wastewater, heavy metals are known to be toxic, non-biodegradable and have long half-life [2]. The existence of heavy metals in contaminated water has been a matter of interest to the public because of their toxicity effect in the discharging environment [3]. Elimination of these heavy metals from wastewater has become a point of concern, especially in places where recycling of the water is mainly practiced, the recovery of these heavy metals from wastewater is a significant environmental debate in recent time [4]. Treatment of wastewater containing heavy metals can be accomplished through conventional treatment techniques such as ion exchange, floatation, chemical precipitation, membrane filtration, electrochemical process, adsorption and biological systems [5-10]. These techniques were found to have some drawbacks, which includes incomplete metal removal, production of excess toxic sludge which requires special disposal method, high initial and operation cost, and demand for high energy [11]. Lately, several channels have been explored for the formation of inexpensive and more efficient technologies; this is to reduce the quantity of wastewater generation and also to enhance treated effluent quality. Adsorption method was found to be one of the most suitable substitutes for wastewater treatment compared to the existing treatments. Commercial activated carbon (AC) is the most effectively and widely used adsorbent in the adsorption process. Application of AC in the adsorption process was found to have some setbacks. AC is found to be very expensive; its cost is related to its quality, the finer it is, the more costly it becomes. Recently, the search for inexpensive adsorbents with the ability

for metal binding has been strengthened [12]. The adsorbents can be of agricultural waste, industrial by products, biomass, biological and organic origin, polymeric materials and zeolites [13]. In this study, sugarcane bagasse activated carbon (SCBA) was produced as an adsorbent through thermal incineration process. Adsorption experiments were conducted to investigate the possibility of using SCBA as an alternative adsorbent for removal of lead ions from aqueous solution. Parameters such as initial pH of the solution and SCBA dosages were investigated to find their effects on the adsorption of Pb^{2+}.

2. Material and methods

2.1 Preparations of adsorbent material (SCBA)

Sugarcane bagasse was collected from a local outlet (Pasar Malam) night market at Seri Iskandar, Tronoh, Malaysia. The bagasse was manually cut to the average size of 3 cm and thoroughly washed with tap water to remove ligneous, cellulose and trapped impurities. Bagasse was further washed with deionized water to achieve further purity and for decontamination purpose. The purified bagasse was then dried in an oven at 105 ℃ for a period of 24 hours until constant weight was achieved. 10 g of the dried bagasse was weighed and placed in a tube furnace; the furnace was then heated to a temperature of 900 ℃, at a heating rate of 10 ℃/min. The furnace temperature was maintained at 900 ℃ for 3 hours. Nitrogen gas at a flow rate of 100 mL/min was used as inert gas to deplete oxygen within the system. The resulting material (SCBA) was then grinded and made into powder form with an average sieved size of 150 μm. SCBA was then pulverized and immersed in a weak acid (0.5% H_2SO_4, pH 4.25) at room temperature for 24 hours; this was to ensure the adsorbent is kept within an acidic state. The material was filtered from the solution, washed and dried in an oven at 70 ℃. SCBA was stored in an airtight container before use.

2.2 Preparation of adsorbate solution

A stock solution of lead chloride (Pb^{2+}) was prepared by dissolving its calculated weight of salt in 1 L of distilled water to obtain a concentration of 1000 mg/L. Further working concentrations were obtained by diluting the stock solution to the required strength. The chemical employed are of analytical grade, obtained from Merck (Germany).

2.3 Experimentations

Series of 250 mL Erlenmeyer flasks containing 100 mL of synthetic Pb^{2+} solution at predetermined concentrations and 0.5 g SCBA dosage were used in the adsorption experiments. An orbital shaker (Protech Model 722) was used to agitate the flasks at a constant speed of 150 rpm at room temperature (26 ± 1 ℃), for a scheduled period of time. At the end of the scheduled agitation time, the flasks were removed from the orbital shaker and the mixture was filtered through Whatman's glass microfiber filters paper (GF/C). Atomic Absorption Spectrophometer, AAS (Model AA 6800 Shimadzu) was used to analyze the filtrate for residual Pb^{2+} concentration in mg/L.

The effect of pH on the adsorption of Pb^{2+} was studied by varying the initial pH of the solution in the range of pH 1 to pH 8. The pH of the solution was adjusted using either 2.0N HCl or 1.5N NaOH. Other parameters such as initial Pb^{2+} concentration, contact time, adsorbent dosage and agitation speed were kept constant at 10 mg/L, 2 hrs, 0.5 g and 150 rpm, respectively. The pH of the solution was measured using a pH meter (Model EW 53013, Hach Sension 1).

Batch experiments were also carried out to investigate the effect of SCBA dosages on the adsorption of Pb^{2+} ions. The SCBA dosage was varied from 2 g/L to 16 g/L until equilibrium Pb^{2+} removal was achieved. The pH of the solution was initially adjusted to the optimum value obtained. Other parameters such as contact time, initial metal concentrations and agitation speed were fixed at 3.5 hrs, 100 mg/L and 150 rpm, respectively. At the end of the scheduled time, the mixture was filtered and analyzed for residual Pb^{2+} concentration in mg/L. Eq. 1 and Eq. 2 were used to compute metal adsorption efficiency and adsorption capacity of SCBA, respectively.

$$R = \frac{(C_i - C_e)}{C_i} \times 100\% \qquad (1)$$

where, R is the Pb^{2+} removal efficiency (%), Ci is the initial Pb^{2+} concentration and Ce is the residual Pb^{2+} concentrations (mg/L) at equilibrium.

$$Q_c = \frac{(C_i - C_e)V}{W} \qquad (2)$$

where, Q_c is the adsorbent adsorption capacity (mg/g), C_i is the initial Pb^{2+} concentration and C_e is the residual Pb^{2+} concentration (mg/L) at equilibrium, V is the volume of aqueous Pb^{2+} solution (L) and W is the mass of SCBA (g).

2.4 Adsorption isotherms studies
Freundlich isotherm model is a commonly used model for describing adsorption equilibrium based on the empirical equation. Freundlich isotherm model has the ability to unfold adsorption related to both organic and inorganic composites on a wider range of adsorbents inclusive of biosorbent [14]. Freundlich isotherm model can be written in the following linearized form of Eq. 3 [15].

$$\log A_q = \log K_F + \frac{1}{n} \log C_e \qquad (3)$$

where $\log A_q$ is the quantity of the adsorbed pollutant per gram of the adsorbent (mg/g), C_e is the equilibrium concentration (mg/L), K_F and n are Freundlich constants. The plot of $\log A_q$ against $\log C_e$ has *1/n* as slope and $\log K_F$ as its intercept.

Langmuir model is another frequently used model which describes heavy metals sorption unto biosorbent. Langmuir model operates based on three distinct assumptions viz; that all surface sites are the same and can occupy one adsorbed atom, it is limited to monolayer coverage adsorption and capability of a molecule adsorbed at a given site is not dependent on the occupancy of its adjoining sites [14]. Eq. 4 below describes Langmuir isotherm model in its linear form [16].

$$\frac{C_e}{A_q} = \left(\frac{1}{K_L}\right)\left(\frac{1}{b}\right) + (C_e)\left(\frac{1}{b}\right) \qquad (4)$$

where A_q is the quantity of pollutant adsorbed per gram of adsorbent (mg/g), K_L is the Langmuir constant for equilibrium, b is the adsorbate quantity that is required for a monolayer formation and C_e is the concentration of residual metal at equilibrium (mg/L). Thus, the plot of C_e/A_q against C_e will be a straight line with a slope of $1/b$ and intercept of $1/K_L$.

3. Results and discussions
3.1 Effect of initial pH
This experiment was conducted to investigate the effect of initial pH on the removal of Pb^{2+} using SCBA. Figure 1 shows the plot of Pb^{2+} removal efficiency against initial pH of the solution.
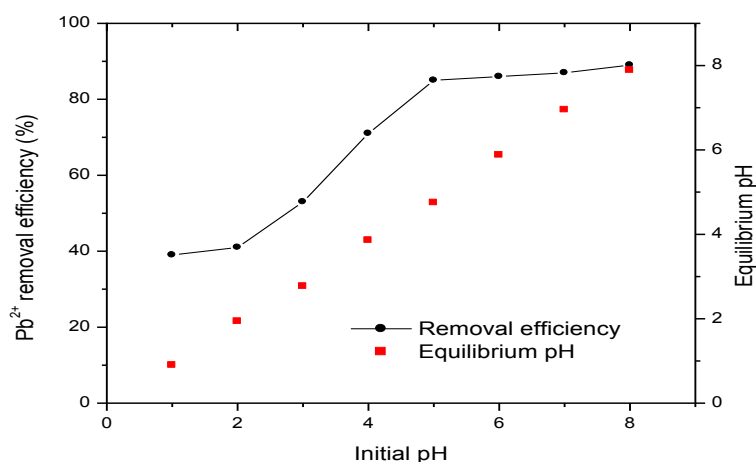
Figure 1. Pb^{2+} removal efficiency against initial pH (Pb^{2+} concentration 10 mg/L, contact time 2 hours, speed 150 rpm, adsorbent dosage 5 g/L and temperature 26 ± 1 °C).

From Fig. 1, it can be observed that Pb^{2+} removal efficiency increased with increasing pH of the solution. At lower pH level, the removal efficiency is low compared with higher pH level. This was because of the presence of high concentration of hydrogen ions (H^+) at lower pH compared to their less concentration at higher pH level. As the pH of the solution was increased, the SCBA surface becomes more negatively charged, as such, the electrostatic attraction between the SCBA surface and the Pb^{2+} ions increased. This led to the adsorption of more Pb^{2+} ions and the release of H^+ ions from the SCBA surface back into the solution. At the end of the experiments and for all the samples, the final pH of the solutions was found to be less than the initial pH values. The changed in pH was due to the ion exchange process that took place between the hydrogen ions and the lead ions as the pH was increased. Qaiser et al. [17] reported that lead usually present as Pb^{2+} at a pH range of 2 to 6, and at pH above 6.0, it will hydrolyze to $Pb(OH)_2$ and $PbOH^+$ [17]. For this reason, the pH value of 5.0 was considered to be optimum and was used in the study of the effect of adsorbents dosages on the adsorption of Pb^{2+} ions by SCBA.

3.2 Effect of adsorbent dosages
This experiment was conducted to investigate the effect of SCBA dosages on the removal of Pb^{2+} from aqueous solution. The results obtained were plotted in Fig. 2 below.
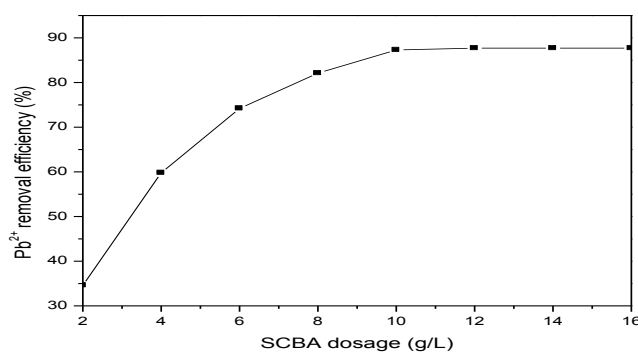

Figure 2. Pb^{2+} removal efficiency against SCBA dosages (Pb^{2+} concentration 100 mg/L, contact time 3.5 hrs, agitation speed 150 rpm, pH 5.0 and temperature 27 ± 1 °C).

From Fig. 2, it can be observed that the removal of Pb^{2+} ions increases with increase in the SCBA dosages from 2 to 10 g/L . This was due to the presence of more active sites and large surface area of SCBA that are readily available and easily be accessible for Pb^{2+} ions adsorption. The incremental removal of Pb^{2+} ions was not significant when the SCBA dosage was increased beyond 10 g/L. At this stage, it was expected that the concentrations of Pb^{2+} ions at the surface of SCBA and the concentrations of the Pb^{2+} ions remaining in the solution are in equilibrium with each other. SCBA dosage of 10 g/L was considered to be optimum for this study. The corresponding removal efficiency was found to be 87.3%. This was in accordance with the result reported by Ribeiro et al on the removal of Pb^{2+} using modified egg shell waste [18].

3.3 Adsorption isotherms studies (performance of SCBA)
This study was carried out to establish the relationship between the concentration of Pb^{2+} ions and its degree of adsorption onto the surface of the SCBA adsorbent at a fixed temperature. The adsorption isotherm constants obtained from the plots of the linearized Langmuir and Freundlich models are presented in Table 1.

Table 1 Langmuir and Freundlich isotherm for Pb^{2+} and its comparison with other studies

Adsorbent	Langmuir				Freundlich			Reference
	Q_o	b	R^2	R_L	K_F	R^2	$1/n$	
SCBA	**23.4**	**0.29**	**0.9508**	**0.26**	**1.73**	**0.8629**	**0.52**	**This study**
Cedar leaf ash	7.23	0.17	0.998	N/E	1.56	0.992	0.43	[19]
Peat	82.31	0.45	0.992	N/E	18.72	0.525	0.54	[20]

From Table 1, it can be seen that coefficients of determination (R^2) for SCBA from the Langmuir isotherm model was found to be 0.9508. This indicates that Langmuir isotherm model satisfactorily described the adsorption of Pb^{2+} onto SCBA. This indicates the monolayer coverage of Pb^{2+} ions on the homogenous surface of SCBA. The Langmuir equilibrium parameter R_L value for SCBA was found to be 0.26. This is within the range for favorable adsorption ($0 < R_L < 1$) [21]. The maximum uptake capacity for SCBA was found to be 23.4 mg/g. This is better than some of the adsorption capacities for agricultural by-products reported in the literature. It can be seen that the Freundlich R^2 value from SCBA was found to be 0.8629, (Table 1). This indicates that the adsorption data was not sadequately described by Freundlich isotherm model. The adsorption intensity *1/n* value for Pb^{2+} ions adsorption was found to be 0.52. This indicates a favorable adsorption process with increasing adsorption capacity and the appearance of new adsorption sites [22]. The Freundlich and Langmuir expressions for the removal of Pb^{2+} ions by SCBA are shown in Eqn. 5 and Eqn. 6, respectively.

Freundlich equation,

$$q_e = 1.73 C_e^{0.52} \tag{5}$$

Langmuir equation,

$$q_e = \frac{6.77 C_e}{1 + 0.29 C_e} \tag{6}$$

4. Conclusions

The present study has shown that activated carbon produced from the sugarcane bagasse (SCBA) using tube furnace can be engaged as an environment friendly and low cost adsorbent for the removal of Pb^{2+} ions from synthetic aqueous solution. The study on the effect of pH revealed that the competition between H^+ and metal ions at low pH values is the main leading factors that affect the adsorption characteristics of SCBA. Optimum removal efficiency was achieved at pH 5.0. The number of adsorption sites increased due to an increase in SCBA dosage and optimum removal efficiency of 87.3% was achieved at SCBA dosage of 10 g/L.

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