

Ashed SBE Adsorbent for Lead and Zinc (II) Ions: Kinetic and Equilibrium Studies

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Abstract: *The present study investigated the adsorption potential of Ashed SBE (spent bleaching earth) to remove lead (II) and zinc (II) ions from industrial effluent. The effluent was found to have a higher percentage of lead (II) and zinc (II) ions beyond the acceptable WHO (World health organization) standards. The maximum adsorption capacity was found to be 29.8 and 43.4 mg/L for adsorption of lead (II) and zinc (II) ions respectively. Lead and zinc (II) ions removal was mainly influenced by the operating variables of the solid/liquid ratio and the pH of the aqueous phase. The kinetic data was evaluated and the pseudo-second-order equation provided the best correlation. The present study demonstrated that ASBE is a promising material that may be used for the removal of heavy metal ions from industrial effluents.*

Keywords: Adsorption; Ashed SBE; Isotherms Kinetics, Lead (II) and Zinc (II) ions.

1. Introduction

The use of various adsorbents for the removal of heavy metal ions from aqueous solution is of great interest due to environmental concerns. Lead and zinc are widely used in many industrial applications. Lead is used battery cells, paints, manufacturing, printing pigments, and fuels among others [1]. Lead exposure causes weakness in fingers, wrists and ankles. The effects of lead toxicity are very wide and include impaired blood synthesis, hypertension, severe stomach ache, brain, kidney damage and even can cause miscarriage in pregnant women [2]. Zinc is used in a variety of industrial products. For example, Zinc Oxide is used as a sunscreen agent. It reflects and scatters UV radiation. Sunscreen products reduce or prevent sunburn and premature aging of the skin. Preventing sunburn is an important factor in reducing the risk of getting skin cancer. Zinc citrate is used in toothpaste and mouthwash [3]. Excessive zinc intake suppresses copper and iron intake. This can lead to nausea, vomiting, pain, cramps and diarrhea may occur. There is also a condition called the "zinc shakes" or "zinc chills" or metal fume fever that can be induced by the inhalation of freshly formed zinc oxide formed during the welding of galvanized materials [4]. The removal of heavy metals from contaminated water bodies has been attempted by several scientists employing a wide variety of techniques. These include chemical precipitation, ion-exchange, electro flotation, membrane filtration, reverse osmosis and so on. All these methods are generally expensive. For this reason, there is a need to develop economic and eco-friendly methods for heavy metal ions removal. Currently SBE is dumped in open fields within operation areas of oil processing factories, in Kenya. There is need for investigation on its suitability as an adsorbent. Most of the research has been done used simulated water. It is important to use the real industrial wastewater. In this paper, we describe our efforts to remove lead (II) and zinc (II) ions from industrial effluent using ashed SBE. The adsorption of metal ions was investigated with variations in the parameters of pH, contact time, initial

metal ions concentration and temperature.

2. Modelling and Analysis of Batch Data

The equilibrium relationships between adsorbent and adsorbate are best explained by sorption isotherms [5]. They describe the relationship between the mass of the adsorbed component per biosorbent mass and the concentration of its component in solution. Determination of equilibrium parameters provides important information used in designing of adsorption systems [6]. The performance and the absorbent ability for absorbing the lead and zinc (II) ions aqueous solution were evaluated by Langmuir and Freundlich models. Temkin and Dubinin-Raduskevich were also used in providing information on the heat of adsorption and verifying results from Langmuir and Freundlich isotherms [7]. The Langmuir equation may be formulated as

$$q_e = \frac{bQ_{\max}C_{eq}}{1 + bC_{eq}} \quad (1)$$

Where q_e corresponds to the amount of solute ions, C_{eq} is the solute concentration in aqueous solution after equilibrium is reached, Q_{\max} represents practical limitation adsorption capacity, b is an affinity constant for binding sites. A high value of b indicates a high affinity of the biosorbent for the sorbate. The essential characteristics of the Langmuir equation can be expressed in terms of a separation factor R_L which is a dimensionless constant given by equation 2 [8].

$$R_L = \frac{1}{1 + Q_{\max}C_o} \quad (2)$$

Freundlich is an empirical isotherm model that considers heterogeneous adsorption on the adsorbent surface and is given by equation 3.

$$q_e = K_f C_e^{\frac{1}{n}} \quad (3)$$

Temkin isotherm assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to species-adsorbate interactions [9]. The linearised equation is given by equation 4

$$q_e = B \ln A_T + B \ln C_e \quad (4)$$

Where A_T is Temkin isotherm equilibrium binding constant corresponding to the maximum binding energy, b_T is Temkin isotherm constant, R is universal gas constant, T is the absolute temperature and B is Constant related to heat of sorption. The magnitude of A_T provides guidance on selection of the adsorbent.

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The model has often successfully fitted high solute activities and the intermediate range of concentrations data well [10]. The model is represented by equation 5.

$$q_e = (q_s) \exp(-K_{ad} \epsilon^2) \quad (5)$$

Where, q_e is amount of adsorbate in the adsorbent at equilibrium, q_s is theoretical isotherm saturation capacity, K_{ad} is the Dubinin–Radushkevich isotherm constant and ϵ is the Polanyi potential.

Kinetics of Biosorption

The adsorption kinetic studies describe the solute uptake rate which in turn controls the residence time of adsorbate uptake at the solid-liquid interface. Biosorption kinetics is described traditionally by the pseudo first order model of Lagergren or by pseudo second order kinetics. The linearised pseudo-first order is given by equation 6.

$$\log(q_e - q_t) = \log q_e - \frac{K_L t}{2.303} \quad (6)$$

Where K_L is the Lagergren constant, q_e is the metal adsorbed at equilibrium, q_t is the metal adsorbed at a given time and t is the time taken for the adsorption to take place. The pseudo-second order equation is based on the assumption that the rate-limiting may be chemical adsorption [11]. Linearised pseudo – second order equation is given by equation 7.

$$\frac{t}{q_t} = \frac{1}{K' q_e^2} + \frac{t}{q_e} \quad (7)$$

Where K' is the pseudo – second order rate constant of adsorption, q_e is the metal adsorbed at equilibrium, t is the time taken for the adsorption to take place and q_t is the metal adsorbed at a given time [12].

3. Experimental

3.1 Industrial Effluent

The industrial effluent was sampled into 100 ml plastic bottles and two drops of 0.01M nitric acid were immediately added using a dropper. The effluents temperature and pH were determined on site. The color of the effluent was also noted on site. The samples were transferred to the laboratory and stored in a refrigerator. The effluent was subjected to COD, BOD and turbidity tests.

3.2 Preparation of Adsorbent

SBE was washed several with deionised water. It was ashed in the furnace at 850 °C for 5 hours. After cooling, it was placed in 0.01 M nitric acid then rinsed with distilled water until a pH of 6.5 – 7 was obtained. It was then mixed with 1 M potassium hydroxide in a bomb reactor for 24 hours. The resulting earth ash was then washed with distilled water to a pH of 6.5- 7. It was then oven dried at 80 °C for 5 hours and finally stored in plastic bottles. The ash was subjected to XRD analysis. ppm metal ion in 150 ml plastic bottles placed in a water bath maintained at 25 ± 0.5 °C. The pH was adjusted using 0.01M nitric acid and/or 0.01 M sodium hydroxide. Three samples of 5 ml were collected after five minutes from one bottle at the fifth minute of mixing using a syringe. Thereafter the concentration of metal ions was determined using AAS (Buck, model 210 VGP). All adsorption experiments were carried out in triplicates to check the reproducibility of results. The equilibrium and kinetics data were obtained from batch experiments. The amount of adsorption at equilibrium (q_e) (mg/g) and the percentage adsorption (%) were computed as follows:

$$q_e = \frac{V(C_o - C_e)}{M} \quad (8)$$

$$\text{Percentage adsorption (\%)} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (9)$$

Where, C_o and C_e represented the initial and equilibrium concentrations (mg/L), V is the volume of solution and the M weight of adsorbent (g).

3.3 Batch Adsorption Studies

Batch adsorption equilibrium experiments were conducted for the adsorption of lead and zinc (II) ions on ashed SBE. The effect of contact time, pH, initial metal ion concentration and adsorbent dose were investigated. During the effect of contact time 0.1000 g of test activated adsorbent was mixed with 100 ml of 10 mg/L of Pb (II) or Zn (II) ions solution. Samples of the mixture were withdrawn after every 5 minutes and filtered. The filtrate was tested for the residual metal ions using AAS (atomic Absorption Spectrometry).

4. Results and Discussion

4.1 Characterization

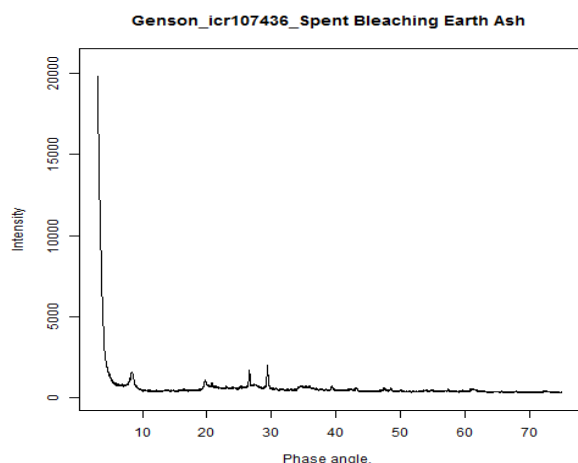


Figure 1: XRD analysis for Ashed SBE

XRD analysis for ashed SBE indicates that it contains 27.6 %, 30.4%, 29.6%, 12.4% of Calcite (CaCO_3), Microcline (KAlSi_3O_8), Palygorskite ($\text{MgAl}_2\text{Si}_4\text{O}_{10}(\text{OH}) \cdot 4\text{H}_2\text{O}$), and Quartz (SiO_2) respectively as the main minerals.

4.2 Effect of Contact Time

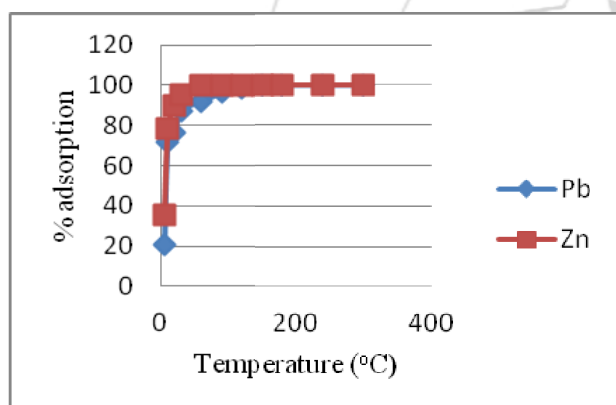


Figure 2: Effect of contact time for adsorption of lead (II) and zinc (II) ions at pH 6.0 and temperature $25 \pm 0.5^\circ\text{C}$.

The rate of adsorption is high at the first 30 minutes after which it slows down. [13], observed that at lower initial metal ion concentration the ions interact with the binding sites fully and almost 100 percent adsorption may take place.

The equilibrium point was reached after 60 and 90 minutes during the adsorption of zinc (II) and Lead (II) ions respectively. [14], found that 60 minutes was sufficient for attaining equilibrium when they studied adsorption of lead (II) ions by activated carbons prepared from marine green algae. They found out that adsorption was rapid and more than 90 % lead (II) ions were adsorbed within the first 30 minutes.

4.3 Effect of pH

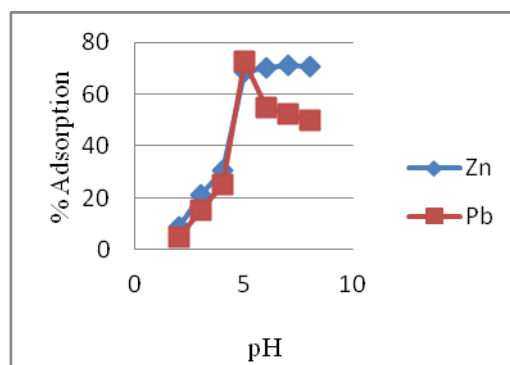


Figure 3: Effect of pH on adsorption of lead (II) and zinc (II) ions at temperature $25 \pm 0.5^\circ\text{C}$

The maximum adsorption for lead (II) ions took place at pH of 5. Above pH 6 there was decrease in lead (II) ion uptake. [14], observed similar results when they investigated adsorption of lead (II) ions from aqueous solutions using activated carbon from marine algae. They suggested that at pH less than 2.5, H^+ ions compete with lead (II) ions for the adsorption sites on surface of the adsorbent. The adsorption of zinc (II) ions continued to increase with the pH. [15], investigating adsorption of zinc (II) ions on kaolinite and metakaolinite, found out that at pH greater than 6.0, the solubility of zinc decreased resulting in their precipitation as hydroxide with no significant increase in percentage adsorption. The results show that adsorption of zinc (II) ions onto the adsorbent considered is pH dependent. The pH of the solution has a significant impact on the uptake of heavy metals, since it determines the surface charge of the adsorbent, the degree of ionization and the speciation of the adsorbate.

4.4 Effect of Sorbent Dosage

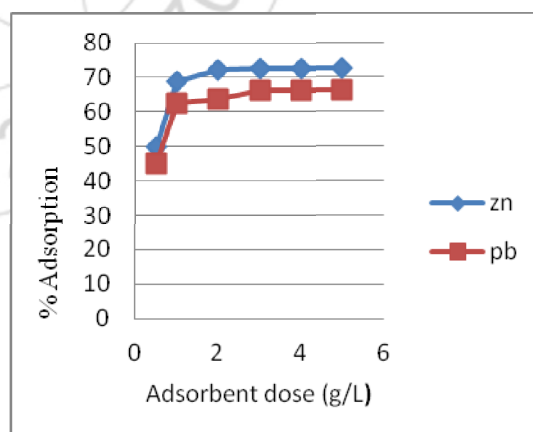


Figure 4: Effect of sorbent dosage on adsorption of lead (II) and zinc (II) ions at initial concentration of 10 mg/L, pH 6.0 and temperature $25 \pm 0.5^\circ\text{C}$.

The results show that there was an increase in the amount of the lead (II) and zinc (II) ions adsorbed According to [16], higher dosage of adsorbent increases the adsorption due to more adsorption sites being available. There was increase in adsorption with the adsorbent dosage was up to a certain amount beyond which further addition of the adsorbent did

not cause any significant change in the adsorption. [17], suggested that this may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles. The results show that there was general increase in the amount of zinc (II) ions adsorbed with the increase in adsorbent dosage. [18] in their study on adsorption of copper and zinc from sulfate media on a commercial sorbent also made a similar observation. This result agrees with what [19] found out during their study on adsorption of Cu (II) ions from regenerated SBE. They suggested that adsorption increased with increasing adsorbent dosage due to increased availability of adsorptive surface. They also found out that although high loading capacities were desirable for sorbent dosages greater than 4 g/L the slurry became too thick to agitate effectively. [20], observed that the decline in adsorption beyond certain adsorbent dosages could be due to the aggregation/agglomeration of sorbent particles at higher dosages which would lead to a decrease in the total surface area of the adsorbent particles available to the metal ions.

4.5 Effect of temperature

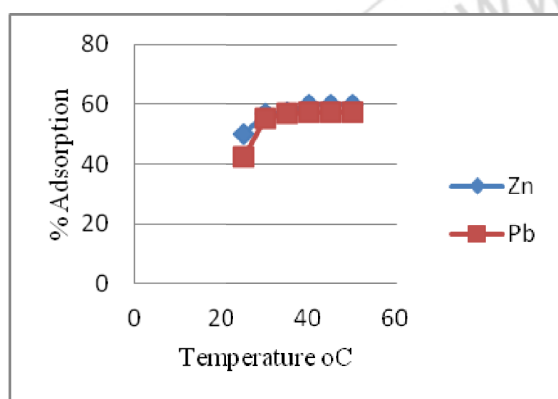


Figure 5: Effect of temperature on adsorption of lead (II) and zinc (II) ions at initial concentration of 10mg/L, pH 6.0 and temperature $25 \pm 0.5^\circ\text{C}$.

The results show that there was an increase in the amount of the lead (II) and zinc (II) ions adsorbed when, the temperature was increased. [21], in their study on adsorption of Zn (II) ions on *Carica papaya* root powder obtained similar results. They suggested that the enhancement of the adsorption capacity when temperature is increased could be due to increased mobility and diffusion of ionic species.

4.6: Effect of Initial Concentration

An increase in adsorption capacity was realized as the initial concentration was increased. This is because a higher metal concentration means a greater driving force for mass transfer from the aqueous solution to the solid adsorbent. [22], in their study on optimization and kinetic modeling of cadmium desorption from citrus peels observed that the biosorption capacity increases with the increasing metal ion concentration. For a given adsorbent dosage, the amount of metal ion adsorbed per unit area of the adsorbent removal of the metal ions decreased with an increase in the initial concentration. According to [23], the adsorbent has a limit number of active sites, and fewer of them are available at equilibrium sorption at a higher zinc loading levels. The

percentage removal however, decreases with increasing metal ion concentration. [24], reported that at higher concentrations, more metal ions are left unabsorbed in solution due to the saturation of binding sites.

4.6: Adsorption isotherms

Figures, 6, 7, 8 and 9 show the fits of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms for adsorption of lead (II) and zinc (II) ions.

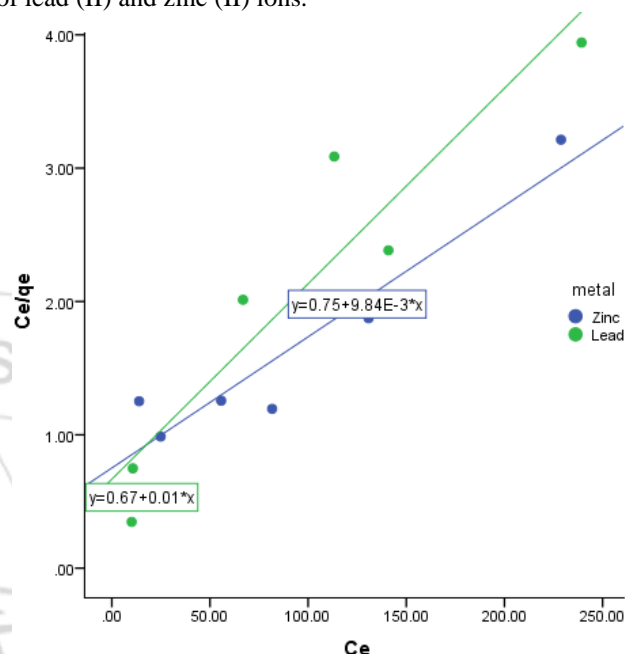


Figure 6: Langmuir biosorption isotherms for adsorption of lead (II) and zinc (II) ions at initial concentration of 10 mg/L, pH 6.0, temperature, $25 \pm 0.5^\circ\text{C}$ and adsorbent dose of 2 g/L.

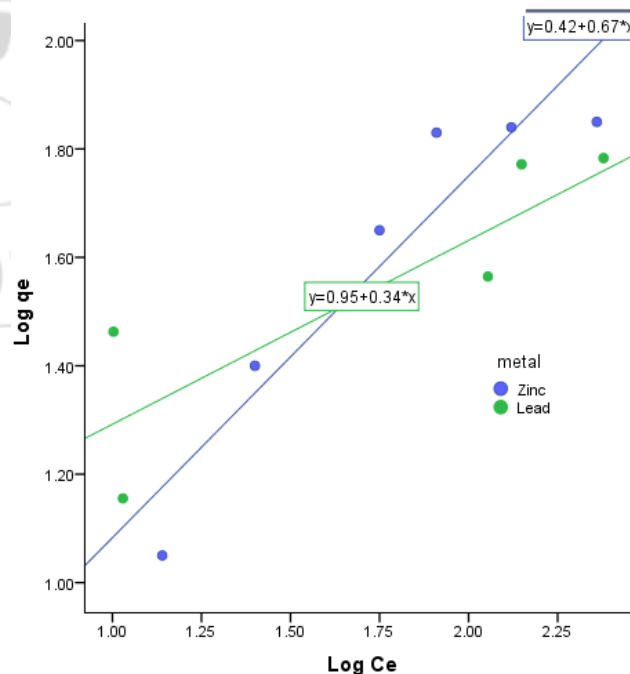


Figure 7: Freundlich adsorption isotherms for adsorption of lead (II) and zinc (II) ions at initial concentration of 10 mg/L, pH 6.0, temperature, $25 \pm 0.5^\circ\text{C}$ and adsorbent dose of 2 g/L.

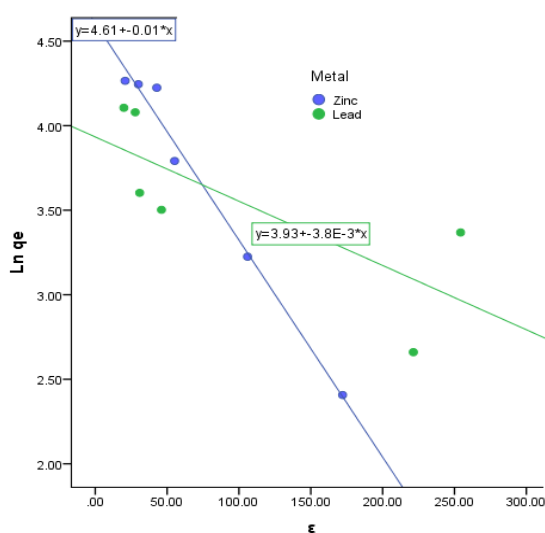


Figure 8: Dubinin-Radushkevich isotherms for adsorption of lead (II) and zinc (II) ions at initial concentration of 10 mg/L, pH 6.0, temperature, $25 \pm 0.5^\circ\text{C}$ and adsorbent dose of 2 g/L.

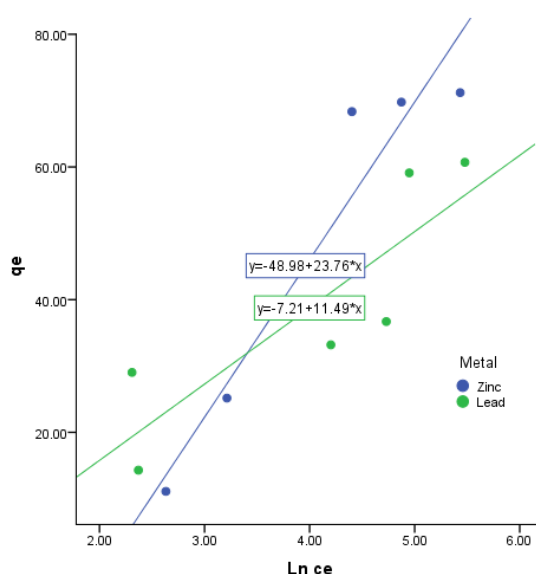


Figure 9: Temkin isotherms for adsorption of lead (II) and zinc (II) ions at initial concentration of 10 mg/L, pH 6.0, temperature, $25 \pm 0.5^\circ\text{C}$ and adsorbent dose of 2 g/L.

The results indicate that the R^2 values for Langmuir fitting for lead (II) and zinc (II) ions adsorption were 1.0 and 0.94 respectively. The R^2 values for Freundlich fit for lead (II) and zinc (II) ions were 0.62 and 0.77. Temkin and Dubinin Radushkevich did not exhibit a good fit. These results suggest that Langmuir fits better than Freundlich, Temkin and Dubinin Radushkevich isotherms. According to [25], high R^2 for Langmuir adsorption indicates surface homogeneity of the adsorbent and monolayer adsorption. The separation factor R_L was found to be between 1 and 10. This suggests that the adsorption is favorable and the material under investigation may be suitable for adsorption.

4.7: Kinetics of lead (II) and zinc (II) ions adsorption

Table 1: Parameters of first order Lagergren and Pseudo second order kinetic models.

First order Lagergren		Pseudo second order	
K_L	R^2	K'	R^2
0.060	0.8973	1.21	0.9995

The linear regression R^2 show that pseudo second order gave a better fit than first order lagergren. According to [26] the metal-biosorbent reactions may be the rate limiting step. They explained that some adsorption sites become more difficult to reach due to their position in deeper pores. The adsorption of the metal ions increases sharply at the beginning of the process followed by a slower uptake as the equilibrium is approached. [27], made a similar observation when they assessed metal sorption by the marine algae. According to [2], the rate of removal of the two ions is higher in the beginning probably due to a larger surface area of the adsorbent available.

Conclusions

The results of this work indicate that ASBE is a promising material for sequestering heavy metal from industrial effluents. The adsorption data fitted the Langmuir model and the maximum adsorption capacities were found to be 43.4 and 29.79 q_{\max} Mg/g during adsorption of lead (II) and zinc (II) ions respectively at $25 \pm 0.5^\circ\text{C}$. Kinetic analyses showed that the adsorption followed a pseudo second order.

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