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Adsorption of Lead (II) ion from Aqueous Solution using Eggshell Adsorbent

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ABSTRACT

In this study, the efficiency of eggshell adsorbent in removal of Lead (II) ion from its aqueous solution was investigated. Standard experimental procedures were used in conducting the experiment. Results show that chemical composition of eggshell indicated high carbon content of 85.58% which is characteristic of good adsorbent, particle size ranged between 0.075 to 4.750 mm which is evidence of large surface area for effective adsorption. Optimum dosage of adsorbent was 0.3 g corresponding to 76.479% removal. Optimum pH of 6.5 was observed at 84.3% removal. The adsorption process has a very good fit for the Redlich-Peterson isotherm with R^2-value of 0.9920, while scanning electron microscopy (SEM) and Fourier transform infrared spectra both for unloaded and loaded adsorbent show clogged pore spaces in SEM. The disappearance of some functional groups in the FTIR spectra of loaded adsorbent, such as the amine, carboxylic acid, alkyl and aromatic groups, alkanes, aldehydes, terminal alkyne, carbonyl stretching vibration of either α or β-unsaturated aldehydes and ketones show that significant adsorption has taken place. It is concluded that eggshell is a good adsorbent and can be used in tertiary treatment of wastewater.

1. INTRODUCTION

The deterioration of the environments is no doubt a concern to every environmental stakeholder, and this is tremendously increasing at alarming rate due to the quest for development and sustenance of the economy. Advancement in technology and increase in industries are among factors responsible for environmental pollution. Other sources of environmental pollution include population explosion, increase in energy utilization, and waste generated from agriculture, healthcare facilities, landfills, automobile workshops and other municipal activities (Igwe and Abia, 2007; Abdullah and Choudhary, 2017). The industry contributed an enormous number of pollutants released into the environment (Ibrahim *et al*., 2016; Duru and Duru, 2017; Budi *et al*., 2018; Ujile and Okwakwam, 2018). Electroplating and metal producing industries, wood processing industries, petroleum refinery, dye manufacturing industries, amongst others (Ibrahim *et al*., 2016; Ujile and Okwakwam, 2018), are notable industries that pollute the environment. The degree of environmental impact depends on the properties and amount of pollutant released, as well as the nature and type of industry (Al Zubaidy *et al*., 2015; Cirne *et al*., 2016; Fingas, 2018). Wastes or effluents from these industries contain inorganic and organic contaminants such as heavy metals, total petroleum, and poly aromatic hydrocarbons contents (Cirne *et al*., 2016; Abdullah and Choudhary, 2017; Dagde and Ndaka, 2019). Ejection of untreated or partially treated wastes on land and water

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environments impairs on surface water and groundwater quality.

Appropriate waste disposal strategies in most developing countries are not in practice and have resulted to several environmental challenges (Ujile and Owhor 2018). The pollution of surface water can greatly affect aquatic lives and their sustainability, hindrance to aquatic activities such as fishing and impairment of water quality use for agriculture, industrial and other economic activities (Gogoi *et al*., 2015). However, there are several available technologies for the removal of toxic substances like heavy metals, total solids, organics, and biological contaminants, from wastewater. These include ultra-filtration, reverse osmosis, precipitation, oxidation-reduction, ion-exchange, solvent extraction, electrodialysis, electrochemical coagulation and evaporation (Moussavi and Barikbin, 2010). Though, some of these technologies are capital intensive and are only efficient to some extent (Ideriah *et al*., 2012). Adsorption method has been reported to be more efficient for the removal of contaminants from wastewater (Ndamitso *et al*., 2016; Abdullah and Choudhary, 2017; Budi *et al*., 2018; Dagde and Ndaka, 2019). Adsorption method is simple to operate, environmentally friendly, cost-effective and the adsorbents for its operation are readily available (Ndamitso *et al*. ,2016). As one of the most effective wastewater treatment technologies, it has been widely used for the removal of heavy metals from aqueous solution (Jimoh *et al*., 2012; Ademiluyi and Ujile, 2013; Ujile and Joel, 2013; Ujile and Okwakwam, 2018).

Lead poisoning is a problem that must be addressed because it causes carcinoma in humans, and as a result has to be removed from wastewater before disposal. Also, eggshell is indiscriminately disposed causing environmental problems. Therefore, this paper investigated the efficacy of eggshell adsorbent in the removal Lead (II) ion from its aqueous solution.

2. MATERIALS AND METHOD

2.1 Preparation of Samples

Aqueous solution of Lead nitrate Pb $(NO_3)_2$, was used in this study. For the preparation of aqueous solutions, 5.1 g of Pb $(NO_3)_2$, was dissolved in 1000 ml of distilled water contained in 1-liter volumetric flask, from where required initial concentrations were prepared by appropriate dilutions, while eggshells were obtained from fresh eggs after removing the albumen and yoke. The collected eggshells were transported to the laboratory and prepared for analysis in accordance with the method described by Sharma *et al*. (2016). Adsorption experiment was conducted in accordance with the experimental procedures adopted by Obianyo (2021). The Atomic Adsorption Spectrophotometer (AAS) (Model: UNICO 1100) was used to determine the physicochemical properties of water sample and grinded particles of the eggshells. The particle sizes of the eggshell sample were determined by sieve analysis in accordance with BS 1377 (1975). The morphology of the eggshell adsorbent before and after the adsorption was analysed with the aid of scanning electron microscopy (SEM, FEI ESEM Quanta 200). Series of adsorption analysis were carried out in batches using the One-Factor-At-A-Time (OFAT) experimental approach to investigate the effects of adsorbent dosages, concentration of contaminants, contact time, pH and temperature on adsorption capacity using standard methods.

2.2 Estimation of Adsorption Capacity

The percentage of the adsorbed metals by the eggshell was calculated using the expression

$$\text{Adsorbed metal (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

After the determination of the equilibrium concentration, adsorption capacity of each adsorbent at equilibrium was calculated using the formula.

$$Q_e = (C_i - C_e)\frac{V}{w} \quad (2)$$

For instantaneous adsorption, the adsorption capacity was calculated using the expression.

$$Q_t = (C_i - C_t)\frac{V}{w} \qquad (3)$$

where:

Q_e = Concentration of metal ion adsorbed by solid at equilibrium (mg/g),

Q_t = Concentration of metal ion adsorbed by the solid at time, *t* (mg/g)

C_f = Final concentration of metal ion in the liquid mixture (mg/L)

C_i = Initial concentration of metal ion in the solution (mg/L)

C_e = Concentration of metal ion in the solution at equilibrium (mg/L)

C_t = Concentration of metal ion in the solution at time, *t* (mg/L)

V = Volume of liquid mixture (L)

W = Weight of adsorbent (g)

3. RESULTS AND DISCUSSION

Figure 1 show the chemical composition of eggshell determined using the Atomic Adsorption Spectrophotometer (AAS). Carbon constituted 68.468 g (85.58%) of the total weight of 80 g of eggshell used in the experiment, an indication of high effectiveness of eggshell in tertiary treatment of industrial wastewater.

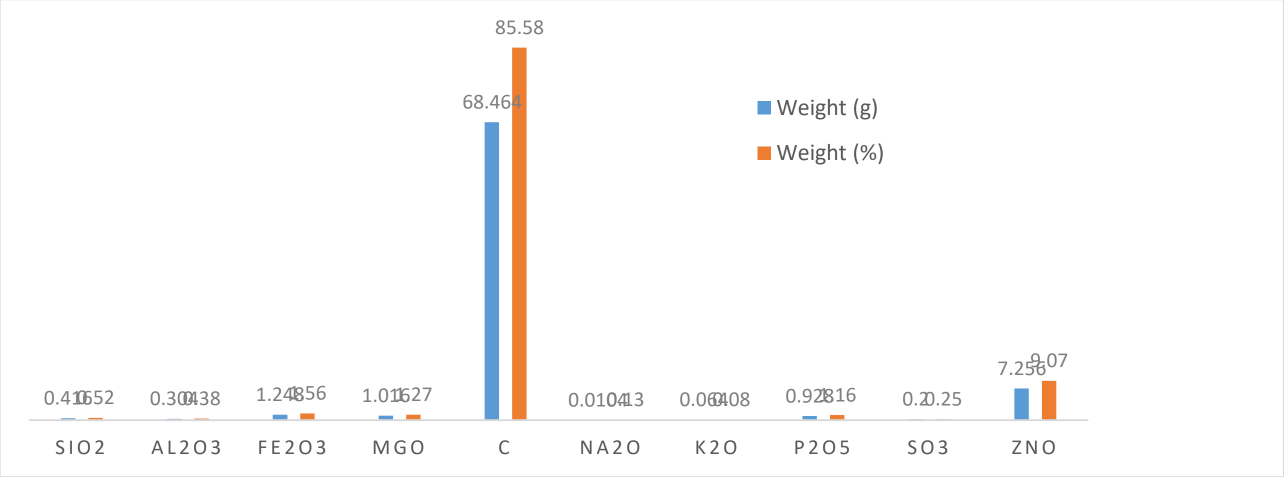


Fig. 1: Chemical composition of eggshell

Figure 2 is the result of the particle size distribution of eggshell adsorbent. It ranged between 0.075 mm to 4.750 mm, smaller particle sizes increased surface area and hence better adsorption (Chen *et al*., 2021).

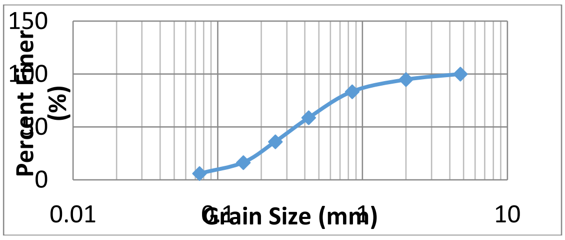


Fig. 2: Particle size distribution of crushed eggshell

From the scan image in Figure 3, microspores of different sizes are evident, which enhanced the adsorption of the Pb^{2+}. However, pores appear clogged after as shown in figure 4. Initial high characteristic peaks of carbon, oxygen, phosphorous and calcium elements present at different energy levels before adsorption decreased after adsorption. shown in figure 6

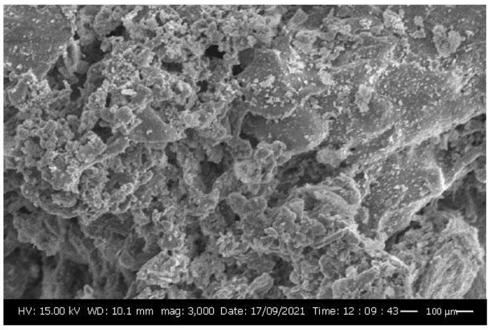


Fig. 3: SEM (morphology) Unloaded

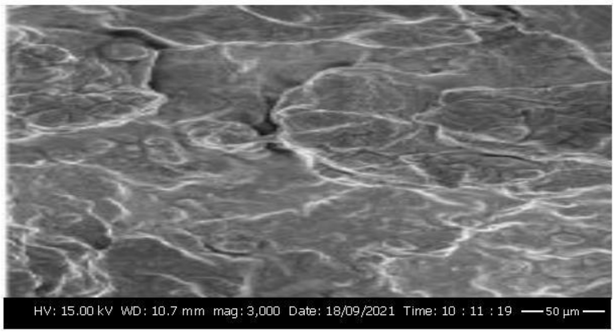


Fig. 4: SEM (morphology) loaded Lead (II) Ion

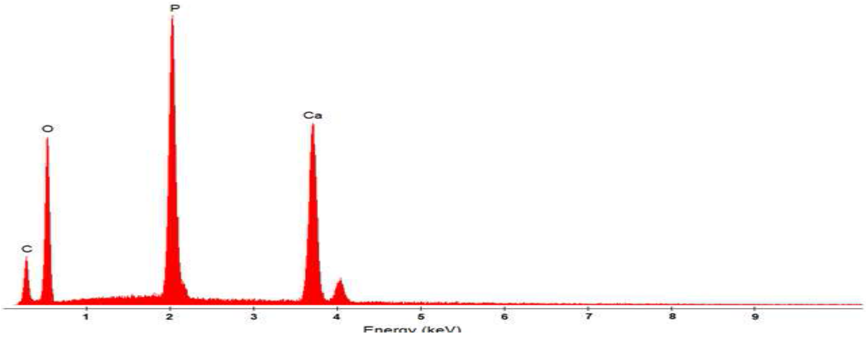


Fig. 5: Characteristic peaks of elements present before adsorption

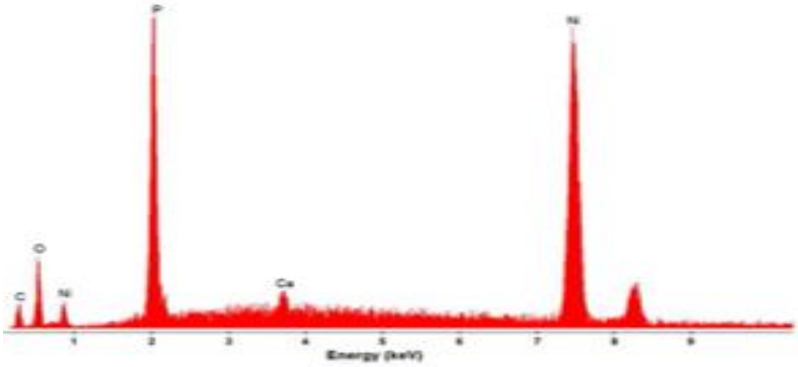


Fig. 6: Characteristic peaks of elements present after adsorption

Figure 7 show the effect of adsorbent dosage on adsorption of Pb^{2+}. Optimum dosage was observed to be 0.3 g corresponding to 76.479 % removal of Pb^{2+} Obianyo (2021) reported insignificant adsorption of Ni^{2+} at small dosages between 0.1 to 0.4 g dosages but increased from values above 0.4 g to 1.0 dosages. Spurthi *et al.*, (2015) reported optimum dosages of 12g/100ml and 8g/100ml respectively for impregnated and non-impregnated rice husk respectively. Mashangwa *et al*. (2017) reported percentage adsorption of Pb^{2+} (96.89 to 98%) as eggshell doses increased from 1 to 7 g with the optimum adsorption recorded at adsorbent dose of 7 g.

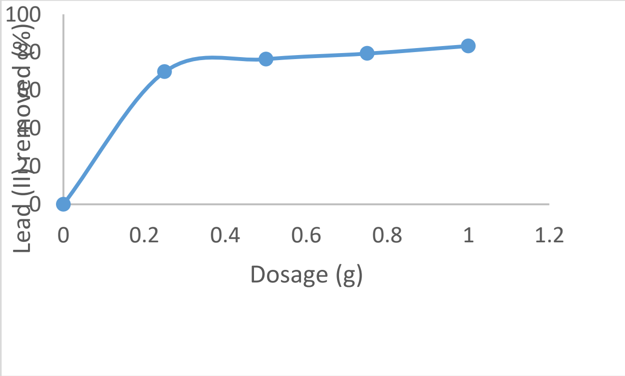


Fig. 7: Effect of adsorbent dosage on adsorption of Lead (II)

In figure 8, optimum pH occurred at near pH of 6.5 corresponding to 84.3% removal of Pb^{2+}. This result indicates that sorption of Pb^{2+} is more pronounced at near-neutral pH, favourable pH occurred between pH of 3 and 6 values as 71.68% Pb^{2+} was adsorbed. No significant increase in adsorption capacity was recorded for adsorption of Pb^{2+} onto the adsorbent after pH of 8 due to hydrozonium ion (H_3O^+) competing with the Pb^{2+} on the adsorption sites of the adsorbents (Mashangwa *et al*., 2017). Also, adsorption capacity was reduced because of repulsion of like charges (Rao and Prabhakar, 2011; Khalili *et al*., 2012), while increase in pH for adsorption of chromium (VI) ions onto egg-shell powder led to decrease in the adsorption of chromium ion (Bamukyaye and Wanasolo, 2017).

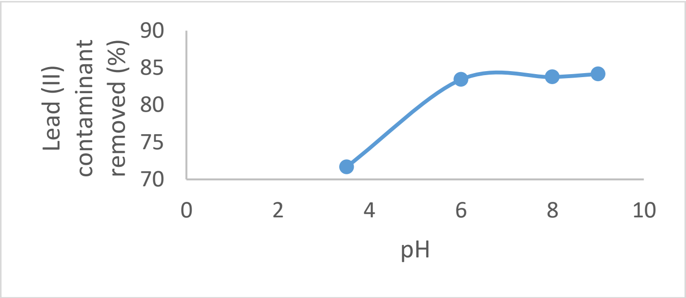


Fig. 8: Variation of Lead (II) Ion adsorbed with pH

Figures 9 to 12 show the Langmuir, Redlich-Peterson, Dubinin-Radushkevich and Temkin adsorption isotherms respectively for sorption of Pb^{2+} from its aqueous solution. The R^2- values for Langmuir, Redlich-Peterson, Dubinin-Radushkevich and Temkin isotherms were 0.9268, 0.9920, 0.8753 and 0.9506 which indicate that adsorption process have a very good fit for Redlich-Peterson isotherm

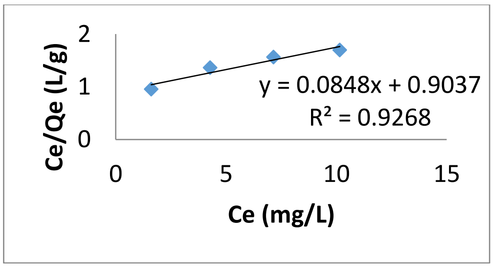


Fig. 9: Langmuir Isotherm for Lead (II) Ion

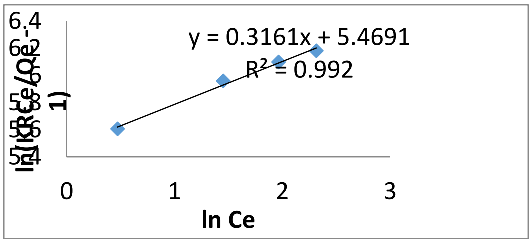
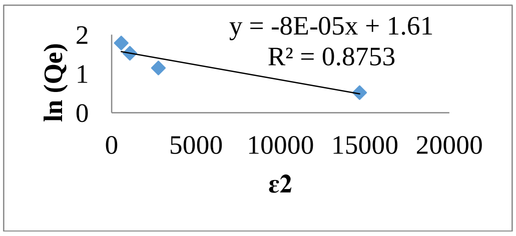


Fig. 10: Redlich–Peterson Isotherm for Lead (II) Ion



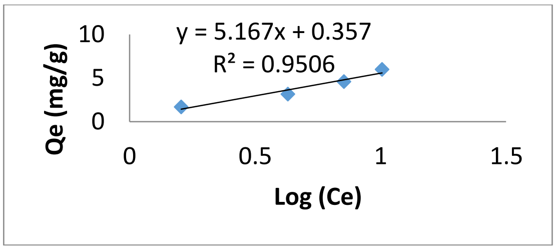


Figure 11: Dubinin-Radushkevich Isotherm for

Figure 12: Temkin Isotherm for Lead (II) **Ion**

Lead (II) Ion

Figure 13 is the FTIR spectrum of transmittance as a function of wave number for unloaded eggshell adsorbent. Wave bands 3857.76 cm^{-1}, 3726.60 cm^{-1}, 3686.43 cm^{-1}, 3417.92 cm^{-1}, 3232.20 cm^{-1} show the presence of single bond amine N-H, and carboxylic acid O-H, stretches respectively. Band 3109.36 cm^{-1} belong to single bond C-H stretching vibration of both alkyl and aromatic groups, while band 2847 cm^{-1} identify with the alkanes C-H stretching vibration. Wave bands 2786 cm^{-1} and 2685 cm^{-1} are indications of O=C-H stretch of the aldehydes, band 2337 cm^{-1} is of the amino-related component NH and band 2114 cm^{-1} is the terminal alkyne, C≡C stretch. Wave band 1820 cm^{-1} is in the category of transition metal carbonyl stretch and wave band 1712 cm^{-1} is for carbonyl stretching vibration C=O, of either α or β-unsaturated aldehydes and ketones in the region of 1730-1735 cm^{-1}, with characteristic high intensity particularly useful for diagnostic purposes. Band 1512 cm^{-1} is for N-O asymmetric stretch and 1373 cm^{-1} belong to the O-H stretch, while bands 1213 cm^{-1} and 1103 cm^{-1} identify with the C-O stretches in the region 1300-1000 cm^{-1}. Bands 896 cm^{-1} and 794 cm^{-1} respectively, belong to strong broad band due to N-H wag usually observed only for primary and secondary amines. These are the functional groups present in the unloaded adsorbent before adsorption of Lead (II) ion started taking place.

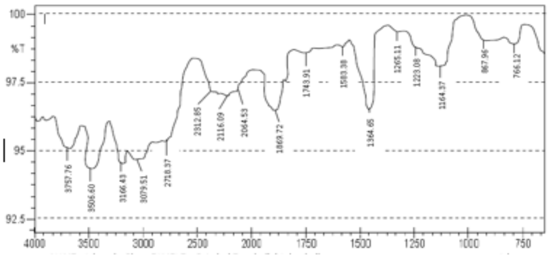


Fig. 13: FTIR spectra of unloaded eggshell adsorbent

The FTIR spectrum of absorbance as a function of wave number for loaded adsorbent is shown in figure 14, in which old peaks disappeared and new peaks appeared. Broad band 3421.67 cm-1 is evident of the conservative nature of adsorption of N-H amine stretch. The new characteristic peaks are 1675.75 cm^{-1} of C=O amide stretch, 2790.33 of C-H aldehyde stretching vibration, the isothiocyanate N=S=S stretching with wave band 2096.14 cm^{-1}. Also present are the C=N stretch, though a shift occurred in this band from 1675.75 cm^{-1} to 1649.09 cm^{-1}, and finally the wave band 1320.53 cm^{-1} which is the fluorocompound C-F stretching vibration. Disappearance of old peaks signify complete adsorption of these functional groups by the adsorbent, while appearance of new peaks are indications of some unknown reactions in the system.

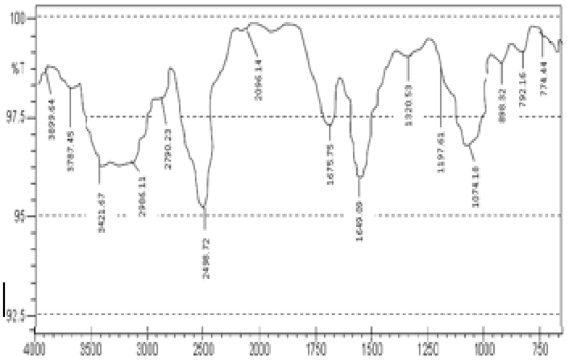


Fig. 14: FTIR spectra of loaded eggshell adsorbent

4. CONCLUSİON

In this paper, adsorption efficacy of eggshell adsorbent in the removal of Lead (II) ion from its aqueous solution is presented. From the results, it is concluded that efficacy of eggshell adsorbent is very high in removal of Lead (II) ions from wastewater. This evident from the chemical composition which showed 85.58 per cent carbon. The SEM morphology and FTIR both for unloaded and loaded also showed that eggshell can serve as a good material for tertiary treatment of wastewater.

Conflict of Interest

The authors declare no conflict of interest

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