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SIMULTANEOUS ADSORPTION OF LEAD AND COPPER USING MODIFIED CHICKEN EGGSHELLS

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Abstract: Water containing heavy metals if not properly treated can lead to serious health implications for humans and animals and severely destroy the environment. The present study investigated the simultaneous adsorptive removal of lead and copper ions from aqueous solutions using modified chicken eggshells (MCE). The eggshells were calcined at 600^{0}C for 2 hours. Optimum conditions obtained were pH 6, adsorbent dose of 15 g and contact time of 90 minutes. Under these conditions, the percentage adsorptions attained were; 96% for lead and 86% for copper. The Langmuir isotherm model fitted the copper adsorption most with a correlation coefficient (R^2) value of 0.9992, while the pseudo second order kinetics fitted the lead and copper adsorption most with R^2 values of 0.9998 and 0.9979 respectively. The efficacy of MCE as a good adsorbent for lead and copper ions is presented as a viable low–cost adsorbent for waste water purification.

Keywords: Modified Egg Shell (MCE), Lead adsorption, Copper adsorption, Kinetics, Biosorbents

INTRODUCTION

Wastewater obtained from sources like tanneries, battery manufacturing factories, mining fields, metal processing industries and so on needs to be properly disposed of to prevent pollution of water bodies, which can in turn alter the growth and development of aquatic organisms. Most common heavy metals found are copper and lead, which when prevalent in high concentrations may be injurious to health and the surrounding environment. Copper is used for various purposes industrially due largely to its good conductive abilities. Copper is carcinogenic and toxic when ingested in large quantities resulting in headaches, vomiting, nausea, liver and kidney failure, respiratory problems and abdominal pain (Ren *et al.*, 2008; Hu *et al.*, 2013; Lan *et al.*, 2013). Lead is toxic, teratogenic and carcinogenic, posing serious health implications to life when exposed to unhealthy quantity. To maintain a safe environment, these metals disposal have to be properly taken care of in the discharged wastewater. There are a variety of methods employed to treat wastewater and extract heavy metals from it, some of these methods include ion exchange, chemical oxidation, reduction, chemical precipitation, adsorption, ultrafiltration, electrodialysis and reverse osmosis (Fu & Wang 2011). Adsorption seems to be one of the most efficient of these techniques.

Biosorbents obtained from biological substances seems cheaper compared to commercial adsorbents. They are not synthetically manufactured, thereby possessing the ability to passively adhere, concentrate and bind contaminants onto their cellular structure. This work will be considering the removal of two heavy metal ions (lead and copper) using modified chicken eggshell. The chicken eggshell is known to possess some distinct mechanical characteristics like impact resistance, excellent blend of stiffness, strength and toughness. It contains about 95% calcium carbonate and 5% organic materials. Modification of the egg shell is usually carried out by calcining at high temperatures. After calcining, the structure changes due to the development of pores as a result of the emission of carbon dioxide gas (Rohim *et al.*, 2014). Simultaneous as well as selective adsorption of lead, copper and some heavy metals onto eggshells and composite formulations had been reported in the literature.

For lead adsorption alone, Vijayaraghavan and Joshi (2013) studied the use of eggshell as an additive to remove lead cations from aqueous solutions in the pH range of 2–5. They confirmed that on reducing the particle size of the eggshell from 750 to 100 microns, the removal efficiency increased from 30.7 to 99.6% using an initial lead concentration of 1045 mg/L. Soares et al., (2016) has evaluated a biosorbent derived from co–composting eggshell (CES) with other organic materials like potato peels, grass clipping, and rice husk, for removing lead (II) ions from an aqueous solution, with about 30 % w/w CES. The CES provided supplementary sites for lead sorption and an increase of about 43 % in the sorption capacity was reported. The efficacy of eggshells for adsorption of lead ions in a hybrid composite formulation with sericite as a binder had been investigated by Choi (2019) with the observation that the adsorption process of lead removal was optimal for adsorbent concentration of 1–1.5 g/L and 30 min mixing time. The removal was well fitted by the Langmuir isotherm model with a correlation coefficient of 0.9963, while the kinetic data were well fitted by the pseudo–second–order model with a correlation coefficient of 0.9982. Hen egg shells (HES) from EnShi, HuBei Province, China, with selenium as a constituent have been used as adsorbent for the adsorption of lead ion from aqueous solutions (Gong et al., 2019).

More recently, chemical surface modification of eggshells using three modifying agents of NaOH, HNO_3 and $KMnO_4$ to produce adsorbents have been investigated for lead removal from aqueous solution with a maximum adsorption capacity of 700 mg/g and removal efficiency of 98% (Basaleh et al., 2020). The development and characterization of magnetic eggshell membranes (MESM) for lead removal from wastewater had been reported by Peigneux et al., (2020). Their results suggested that MESM could be utilized as an efficient nano–remediation agent for lead removal from contaminated waters. As reported, 98.62% maximum

adsorption was obtained by Jamion et al., (2021) for the removal of lead in soil by eggshells activated carbon. The application of synthesized calcium oxide nanoparticles from hen eggshells for the removal of lead ions from aqueous solutions had been investigated (Jalu et al., 2021). The HES was found to remove about 95% of lead from its aqueous solution.

Adsorption of copper alone with eggshell and eggshells formulations had also been investigated. The sorption of copper (II) ions from aqueous solutions by eggshell was investigated by Nõlvak et al., (2013) in a batch experimental system with respect to temperature, initial Cu(II) ions concentrations, pH, and biosorbent doses. The system was best described by the pseudo second–order kinetic with a maximum adsorption capacity of 5.05 mg Cu^{2+}/g eggshell at 25 °C. Waste eggshells for adsorption of copper from synthetic and swine wastewater had been investigated by Hess et al., (2018). From their work, the adsorption of copper followed a second order kinetic model with a theoretical maximum adsorption capacity of 3.0 mgg^{-1} at 20°C. Mohammad et al., (2020) had evaluated the potential of using two types of eggshells of untreated raw eggshells (ES) and eggshells that were mechanically ball–milled into the nano–size (NES), as biosorbents for the removal of Cu(II) ions from aqueous solutions. The NES provided an advantage over ES through much rapid removal of Cu (II). The ES and NES removal efficiencies were 91.36% and 97.21% respectively. A maximum percentage copper(II) removal of about 85% had been confirmed by Madiabu et al., (2021), after Investigating the feasibility of eggshells as a potential adsorbent for copper (II) ion removal from an aqueous solution.

Simultaneous adsorption operation had also been investigated. The feasibility of using magnetic eggshell–Fe_3O_4 powder as an adsorbent for the removal of Pb(II) and Cu(II) ions from aqueous solution with optimal adsorption pH value of 5.5, equilibrium capacity value 263.2 mg/g for Pb(II) and 250.0 mg/g for Cu(II) had been reported by Ren et al., (2012). The removal of lead and copper from textile wastewater using waste egg shells in a continuous stirred tank reactor had been reported by Pandey et al., (2017). The Langmuir isotherm showed the best fitting for the isotherm equilibrium data, with a maximum adsorption capacity of 4.33 mg/g and 3.54 mg/g for lead and copper respectively. Mashangwa et al., (2017) had investigated the adsorptive removal of zinc, lead, copper, and nickel ions from synthetic aqueous solutions and various metals from three acid mine drainage (AMD) sites using chicken eggshells. The percentage adsorptions obtained were 97% for lead, 95% for copper, 94% for nickel, and 80% for zinc. In addition, aluminium, iron, potassium, nickel, and zinc ions all had percentage adsorptions above 75%. Furthermore, potassium had a 98.78% adsorption, while magnesium, strontium, and zinc had 72.33, 68.75, and 53.07% adsorption, respectively. Arsenic, chromium, copper, iron, antimony, and tellurium ions also had above 75% adsorption.

The adsorptive efficacy of eggshell on some other metals with commendable results had been reported. Sasikala et al (2021) has worked on reducing toxic compound extracted from battery waste using activated carbon from Egg shells Nano sized (ES–NP). The ES–NP recorded about 96% removal efficiency. Perchlorate removal efficiency of highly porous nano hydroxyapatite (nHA) and its magnetic composite aerogels (SPIONS@nHA) by freeze–drying technology produced from eggshell had been investigated by Prabhakaran and George (2021). Very fast removal kinetics were observed and the maximum adsorption capacity for nHA and SPIONS@nHA were 148.4 and 305.8 mgg^{-1} respectively. The removal of bismuth ion by 0.45 µm pulverized chicken eggshells had been investigated with optimal removal of 891.29 mg/g by Abbas et al., (2021).

The aim of this study is to simultaneously adsorb lead and copper ions from wastewater onto MCE. The objectives include to study the effect of pH, agitation time, adsorbent weight, adsorbate concentration, and temperature on the adsorption with MCE. Adsorption isotherms like Langmuir, Freundlich, Temkin and Dubinin–Raduskevich as wells as various kinetics will be used to fit the adsorption operation.

METHODOLOGY

All experimental data are averages of three runs. Documented methods were followed (Rajendran and Mansiya, 2011, Rohaizar et al., 2013, Kumaraswamy et al., 2015).

— Materials

These include Simulated wastewater containing copper and lead ions, adsorbent locally sourced from Jekaplay restaurant (chicken eggshells), USA Merck $CuSO_4$≥99.99% 7758–98–7 and USA Merck $Pb(NO_3)_2$ ≥ 99.95%, 10099–74–8 required for preparation of simulated wastewater, USA Merck 37% HCl 7647–01–0 and USA Merck 97% NaOH 1310–73–2.

— Equipment

Switzerland OHAUS Model Explorer Semi micro electric balance, USA Skyray AAS 6000 Flame Atomic Absorption spectrometer, England Pyrex conical flasks (50–500 ml), Germany Witeg Microliter pipettes Witopet premium Starter–Kit 5 402 600 P, India VeeGee 20114–Series Burettes, Timer or a stop watch, United States Carson MicroBrite Plus 60x–120x Power LED Lighted Pocket Microscope (MM–300), England Surgifield Model SM 1002A Muffle Furnace for the calcination of the eggshells, United States Hanna Instruments model HI98107 pH meter, United States Perkin Elmer Fourier Transform Infrared(FTIR) Spectrophotometer Spectrum 2000 Model, Germany Merck KGaA Whatman filter paper no. 41, and Australia RATEK model SWB20D shaker.

— Preparation of simulated wastewater

The wastewater for the procedure was prepared by dissolving lead salts and copper salts in water. USA Merck $Pb(NO_3)_2$≥99.95% salt was utilized alongside copper (II) sulphate ($CuSO_4$). This was carried out by preparing stock solution of 1000ppm, here 3.93g of copper sulphate was dissolved in 1L of deionized water. 1.598g of lead nitrate was

added in 1L deionized water to prepare the 1000ppm stock solution. From the stock solution, a 100ppm concentration of heavy metal contaminated water was prepared. To prepare 5 ppm solution, 100ml was used from 1000 ppm (for Cu & Pb) solution in a beaker and then added to deionized water to top up to 1000ml. A 0.1M HCl or 0.1M NaOH was then used to effectively adjust the pH.

— Pretreatment of eggshells

The locally sourced eggshells were first washed with clean water and then washed with distilled water severally after which, they were left to air dry and then subjected to hot air in an oven at 50 ^{0}C for 2 days. After the drying process was completed, the eggshells were grinded to fine particles with a grinder and then were mixed, it was sieved afterwards to achieve a uniform particle size.

— Calcination of the adsorbent

This modified the eggshells to open the pores thus enhancing adsorption. Different portions of cleaned and crushed powder were put into a metal container and calcined in a muffle furnace at varying temperatures and various time periods. Eggshells were calcined at temperatures ranging between 600 ^{0}C using England Surgifield Model SM 1002A Muffle Furnace with a time period 2 hours at a heating rate of 10 ^{0}C/min.

— Scanning Electron Microscope test

This test was carried out on the eggshell surface to analyze the ultrastructure of the eggshell membrane. This was done by taking up a little portion of the eggshell powder (about 0.5 cm^3) and then mounting on a specimen stub using an adhesive that is conductive in nature, and coated with gold before examination occurs in the electron microscope.

— Fourier Transforms Infrared Spectroscopic Analysis

This test was carried out to study the surface chemistry of the modified eggshells before and after adsorption using spectroscope (FTIR–2000, Perkin Elmer model). FTIR spectra was recorded between 4000 cm^{-1} and 400 cm^{-1}. This was carried out by mixing 1mg of dried eggshell powder with 500 mg of KBr in a mortar and then pressing this mixture at a certain pressure for a time period of 15 minutes. This spectra test gives information about the functional groups on the surface of the modified eggshells.

— Effects of pH on the Cu^{2+} and Pb^{2+} adsorption

The effect of pH on adsorption of Pb^{2+} and Cu^{2+} ions onto eggshell was studied by mixing a given weight of the adsorbent with 100 ml of each 100–ppm individual solution of the adsorbate at different pH values ranging from 4 – 10 at 24^{o}C (ambient temperature). The varied pH value was adjusted using 0.1M NaOH and/or 0.1M HCl solutions and was continually measured by United States Hanna Instruments model HI98107 pH meter. The mixtures were then put on a shaker for time periods varying between 60–90 minutes. The solutions were then filtered through Germany Merck KGaA Whatman filter paper no. 41 (diameter 125 mm) and the filtrate obtained was then analyzed for residual metal concentration. The final concentration of $Pb^{2+}$and Cu^{2+} after the residence time of 90 minutes were measured with the Analyst 400 Perkin Elmer Atomic Absorption Spectrometer (AAS).

— Effects of adsorbate concentration on the adsorption of Cu^{2+} and Pb^{2+} ions

The effect of initial metal concentration on adsorption of Pb^{2+} and Cu^{2+} ions was studied by mixing 0.5 g of the adsorbent with 100 ml of the individual adsorbate (Pb^{2+} or Cu^{2+}) in varied concentrations of 100, 200, 300, 400 and 500 ppm at ambient temperature and pH 7. The individual ion mixtures were then agitated for periods ranging between 60–90 minutes. The solutions were then filtered and analyzed.

— Effects of adsorbent weight on the adsorption of Cu^{2+} and Pb^{2+} ions

The effect of adsorbent dose on the adsorption of Pb^{2+} and Cu^{2+} ions was studied by mixing different masses of the egg shell adsorbent ranging from 2 to 15 g with 100 ml of each 100–ppm individual solution of the adsorbate at ambient temperature and pH 7. The individual ion mixtures were then agitated for a time range between 60–90 minutes. The solutions were then filtered through and analyzed.

— Effects of agitation time on Cu^{2+} and Pb^{2+} adsorption

The agitation on the shaker was decided to be 150 rpm to make the process more efficient for a contact time of 60 minutes and 90 minutes after the pH adjustment and addition of a given weight of adsorbent was done. Afterwards filtration using Germany Merck KGaA Whatman filter paper no. 41 was carried out and then the samples were sent to USA Skyray AAS 6000 Flame Atomic Absorption spectrometer to check the level of adsorption.

3. RESULTS AND DISCUSSION

Figure 1 show the Fourier Transform Infrared spectroscopy of the modified adsorbent (eggshell) after adsorption. It shows sharp declines at 628 cm^{-1} which depicts effects of $CaCO_3$, while those of 1132 cm^{-1} and 1638 cm^{-1} are attributable to the C=O groups. The peak at 3436 cm^{-1} is attributable to H_2O molecules. For most parts of the figure, the spectra after adsorption was lower in value due to the presence of the adsorbed lead and copper ions.

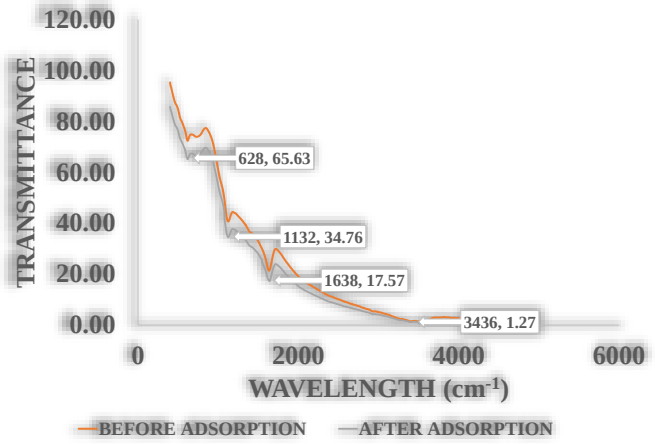

Figure 1: FTIR spectra of the MCE adsorbent before and after adsorption

Figures 2 and 3 show the Scanned Electron Microscope (SEM) image of the MCE adsorbent before and after adsorption

respectively. Figure 3 shows the reduction of the pores sizes and effective surface area after adsorption of the lead and copper ions on the adsorbent.

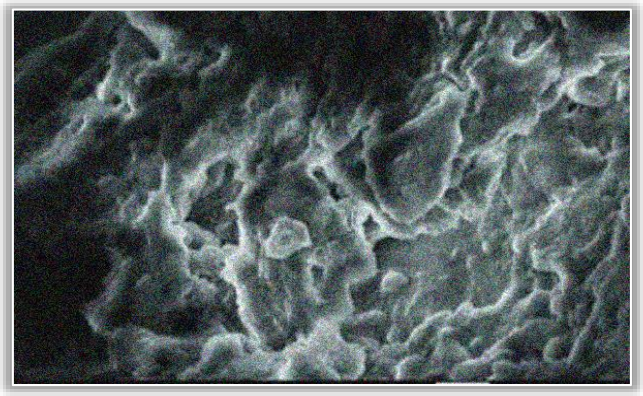

Figure 2: SEM image of the MCE adsorbent before adsorption

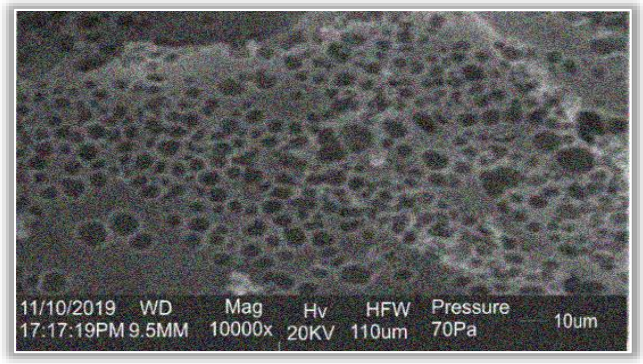

Figure 3: SEM image of MCE after adsorption

— Effect of pH on the adsorption of $Cu^{2+}$and Pb^{2+}ions

The effect of pH on the adsorption capacity of MCE for lead (Pb^{2+}) and copper (Cu^{2+}) is represented in Figure 4. The solution pH was maintained within the range of 4.0 – 10.0. It was noticed that optimum adsorption in this experiment occurred at pH values around 6. At pH 6, the increase in adsorption could be attributed to the weak inhibitory effect of H_3O^+ ions. At pH levels above 6, the adsorption rates were unpredictable due to the accumulation of metal ions on the surface of the adsorbent. A fall in the rate of removal of metal ions at lower pH is due to the higher concentrations of H^+ in the solution which compete with the metal ions for the adsorption sites on the adsorbents. The effect of pH on adsorption was reported by Rohaizar et al. (2013) in a study about the removal of Cu^{2+} from water by adsorption on chicken eggshell. It was found that the adsorption of Cu^{2+} increased as the pH increased from 4 – 7. This displacement reaction creates space for the exchange of ions on the surface of eggshell. Therefore, a pH above neutral is favorable for the effective binding of heavy metals present within the solution. Park et al. (2007) in a simulated study about the removal of heavy metals using waste eggshell, predicted the presence of soluble lead species as $Pb(OH)_4^{2-}$ above pH 12.

Another study, however, reported optimum adsorption of lead ions at pH 6 after which the metal ions started to precipitate (Arunlertaree et al., 2007). This suggests that the optimum pH for the removal of metal ions is dependent on other factors than the acidity or the alkalinity of the solution, which affects the behavior of compounds formed. All metals precipitate as hydroxides by the addition of NaOH and the observed metal removal at these high pH values may also have been due to NaOH and not adsorption onto the adsorbent. Another controlling factor could be the size of eggshell used. This was demonstrated by Pettinato et al. (2015), where they obtained the best results with the smallest particles of the eggshell, owing to the increased surface area available for the adsorption. Although higher percentage adsorption was noted at higher pH values (pH of 8 upwards) for all metal ions, pH 7 was chosen as the optimum pH, as it is the point before adsorption slowed down and also due to environmental considerations where it is environmentally friendly to release neutral aqueous solutions, as opposed to acidic or basic effluents.

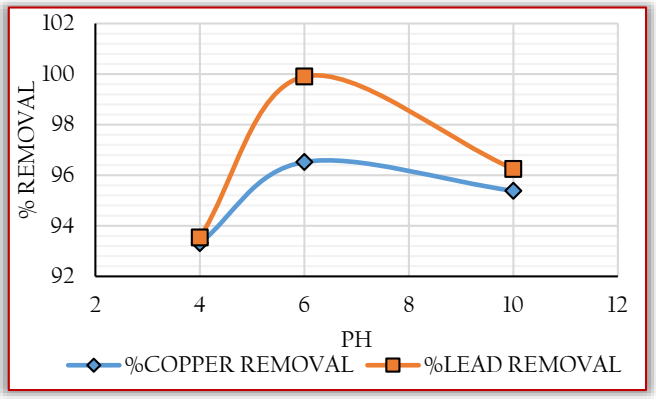

Figure 4: A plot of % metal removal with pH

— Effects of adsorbate concentration on the adsorption of $Cu^{2+}$and Pb^{2+}ions

The effect of adsorbate concentration on the adsorption capacity of eggshells for Cu^{2+} and Pb^{2+} is represented in Figure 5. The analysis on the effect of metal ion concentration demonstrates that an increase in the concentration of lead and copper ions led to a decrease in the percentage adsorption. Anantha and Kota (2016), noticed that the metal ion adsorption of copper increased sharply in the beginning and then decreased slowly with further increase in the initial concentration. This relationship is noted as the initial concentration of lead and copper ions increase. The decline in percentage adsorption may be ascribed to lack of sufficient surface area (1g of eggshell) to allow more metal ions have access to the solution. At lower concentrations most of the ions present can interact with the binding site and thus the percentage adsorption is higher, whereas at higher ionic concentration, the adsorption is low due to the saturation of adsorption sites which is attributed to the increasing number of ions competing for available binding sites on the eggshell. The maximum percentage adsorption of lead ions was found to be 96% at a concentration of 300 ppm. For the copper metal, adsorption was noticed to be the highest at a concentration of 100 ppm after which the adsorption percent decreased slightly but steadily.

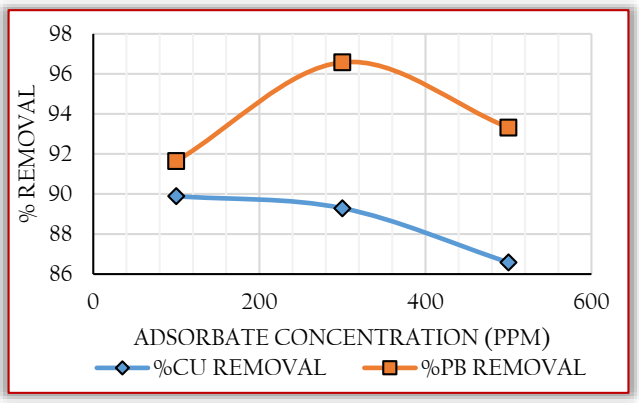

Figure 5: A plot of percentage metal removal with metal ion concentration

— Effects of adsorbent weight on the adsorption of $Cu^{2+}$and Pb^{2+}ions

The effect of adsorbent dose on the adsorption capacity of eggshells for Cu^{2+} and Pb^{2+} is presented in Figure 6. The results represented in the figure show that an increase in the adsorbent dose leads to an increase in adsorption percentage. This is largely due to the increased number of pores that are available for adsorption. Some previous studies reported the removal of lead to be influenced by the dose of eggshell, as the effective removal of solutes increased with increasing dose of adsorbent (Agarwal and Gupta (2014); Agarwal (2012); Arunlertaree et al. 2007). At high sorbent dosage, the available metal ions have adequate exchangeable sites on the eggshell to bind to, resulting in a higher metal ions uptake. Lead showed a very high affinity to the eggshell. It was observed that 1 g of the eggshell was able to adsorb 97.89% of the metal ions.

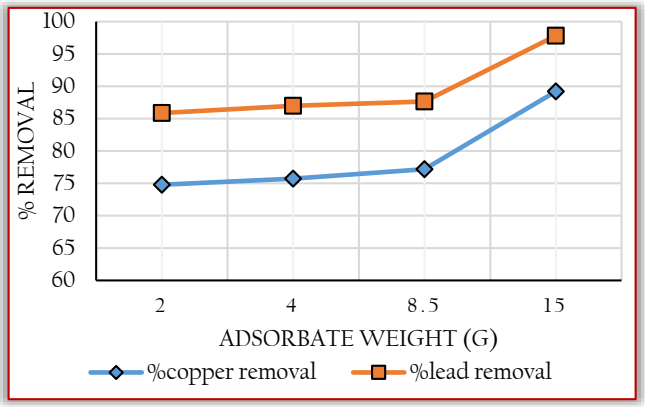

Figure 6: A plot of percentage removal with adsorbent dose

— Effects of contact time on the adsorption of $Cu^{2+}$and Pb^{2+}ions

The effect of contact time on the adsorption capacity of eggshells for Cu^{2+} and Pb^{2+} is represented in Figure 7. The exponential phase for lead was found to be between 60 and 120 minutes, further increase in contact time led to no significant adsorption of metal ions by the eggshell. A slight increase in the percentage adsorption for Cu^{2+} was observed as the contact time increased. Copper indicated a slightly higher increase in percentage adsorption over time. It however dipped at a contact time around 75 minutes, this was due largely to other factors affecting adsorption. The lead ions showed a different trend, as their adsorption reduced with contact time, this can be attributed to the fact that at 60 minutes, the pores available for adsorption had already been filled up, hence any further introduction of adsorbate will only bring about a decline in the percentage metal removal. Similarly, Ipeaiyeda and Tesi (2014) obtained an optimal adsorption for 100 ppm of Pb^{2+} at a contact time between 60 – 120 minutes.

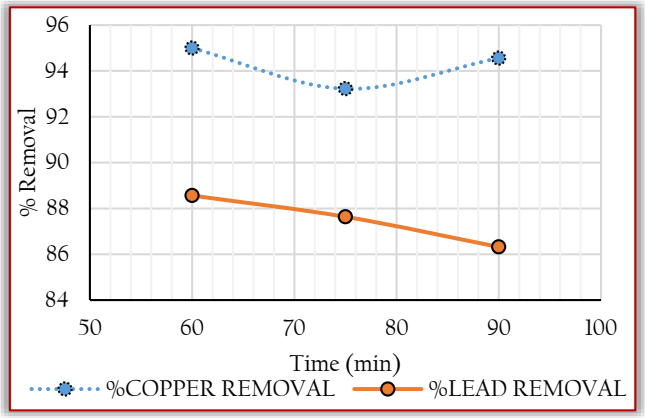

Figure 7: A plot of percentage removal with contact time

— Adsorption Isotherms

The experimental data were tested and compared with the four isotherm models.

≡ Langmuir isotherm

The Langmuir isotherm assumes that the surface of any adsorbent material contains a number of active sites where the adsorbate attaches itself. This attachment can either be physical or chemical. When the attachment is via Van der Waals interactions, it is known as physiosorption and when via covalent bond it is known as chemisorption. It says that there is not much interaction between the adsorbate molecules and once a saturation value has been reached no further adsorption would take place.

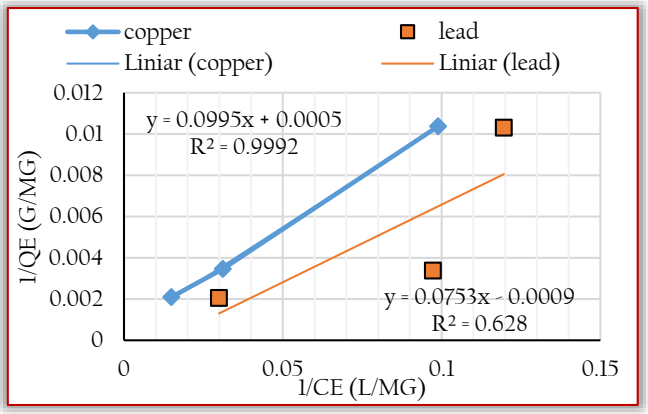

Figure 8: A plot of 1/qe with 1/ce showing the Langmuir isotherm for lead and copper

A linear plot obtained for Langmuir isotherm is shown in Figure 8 for copper and lead.

The Langmuir isotherm equation is given in Equation (1). The equation obtained for the Langmuir isotherm for the current data was obtained from the plot of $1/q_e$ against $1/c_e$.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{C_e}{Q_0} \quad (1)$$

where q_e is the amount of dye adsorbed (mg/g), Ce is the equilibrium concentration of the adsorbate (mg/L), Q_0 is the maximum adsorption capacity (mg/g) and b is the energy of adsorption (J/mol).

≡ Freundlich Isotherm

The Freundlich model is given by Equation 2.

$$\log q_e = \log k_f + {}^1/_n \log C_e \quad (2)$$

where q_e is the amount adsorbed (mg/g), Ce is the equilibrium concentration of the adsorbate (mg/ L), k_f and n, the Freundlich constants are related to adsorption capacity and desorption intensity respectively. The model is based on the assumption that adsorption occurs on a heterogeneous adsorption surface having unequally available sites with different energy of adsorption.

The plots for the Freundlich isotherm for the metal ions (lead and coper) are given in Figure 9.

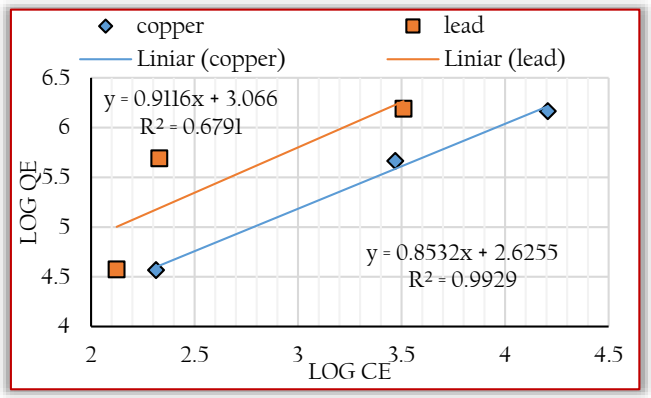

Figure 9: A Plot of log qe with log ce for Freundlich isotherm

≡ Temkin Isotherm

The Temkin isotherm assumes that the heat of adsorption of all the molecules increases linearly with coverage. The linear form of this isotherm is given in Equation (3).

$$q_e = \frac{RT}{b_T} \ln a_T + \frac{RT}{b_T} \ln C_e \quad (3)$$

Qe is the amount adsorbed at equilibrium in mg/g, b is the Temkin isotherm energy constant, T is the temperature, R is the gas constant and a_T is the Temkin isotherm equilibrium binding constant (L/g). The slopes and intercept obtained from the graphical plot q_e against ln Ce were used to calculate the Temkin constants. Figure 10 show a plot of q_e with ln ce for the Temkin Isotherm.

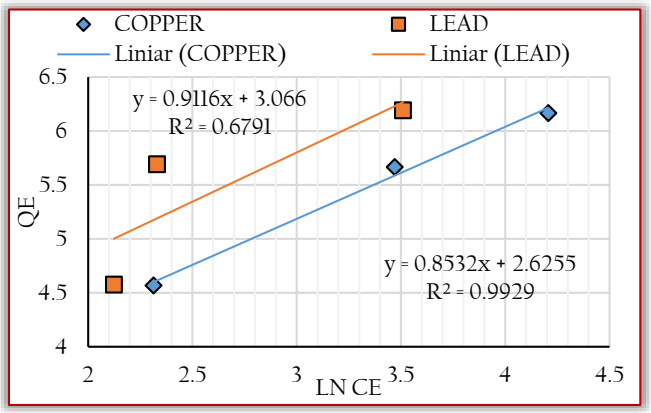

Figure 10: A plot of q with ln ce for the Temkin Isotherm

— Dubinin–Radushkevich Isotherm

The linear form of the Dubinin–Radushkevich isotherm is given in Equations (4), (5) and (6).

$$\ln q_0 = \ln q_D - B\,E^2 \quad (4)$$

where q_D is the theoretical saturation capacity (mg/g), B is a constant related to mean free energy of adsorption per mole of the adsorbate (mol^2/J^2) and ϵ is the Polanyi potential which is related to equilibrium as follows;

$$\epsilon = RT \ln(1 + {}^1/_{C_e}) \quad (5)$$

$$E = {}^1/_{\sqrt{2B}} \quad (6)$$

where ϵ is Polanyi potential, β is the Dubinin–Radushkevich constant, R is gas constant (8.31 J/mol.K), T is absolute temperature, and E is mean adsorption energy.

Figure 11 shows the plot of ln q with E^2 for lead and copper.

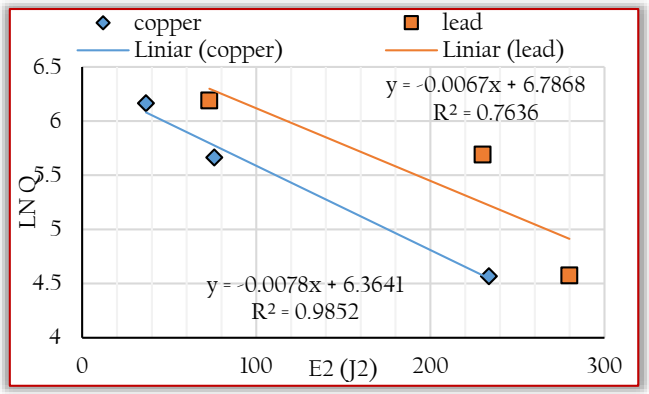

Figure 11: A plot of ln q with E^2

≡ Pseudo First Order Kinetics

This is given in Equation (7).

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (7)$$

Where k_1 (min^{-1}) is the pseudo– first–order adsorption kinetic parameter; q_t is the amount adsorbed at time t (min); and q_e denotes the amount adsorbed at equilibrium, both in mg/g. The plot of log (q_e–q_t) as a function of t provides the k_1 and q_e values as shown in Figure 12.

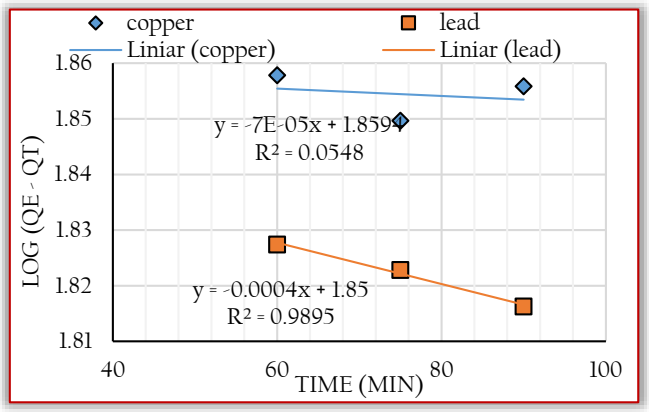

Figure 12: A plot of ln (q_e–q_t) against time

— Pseudo Second Order Kinetics

The pseudo – second–order equation based on the adsorption capacity at equilibrium is expressed in Equation (8).

$$\frac{t}{q_1} = \frac{1}{k_2 q^2_e} + \frac{t}{q_e} \quad (8)$$

where k_2 (g/mg.min) is the pseudo–second – order adsorption kinetic parameter. From the slope and intercept of the (t/qt) as a function of t, k_2 and q_e was obtained in Figure (13). The plots according to Equation (8) provided excellent linearity as R^2 value was 0.9979 and 0.9998 for copper and lead respectively.

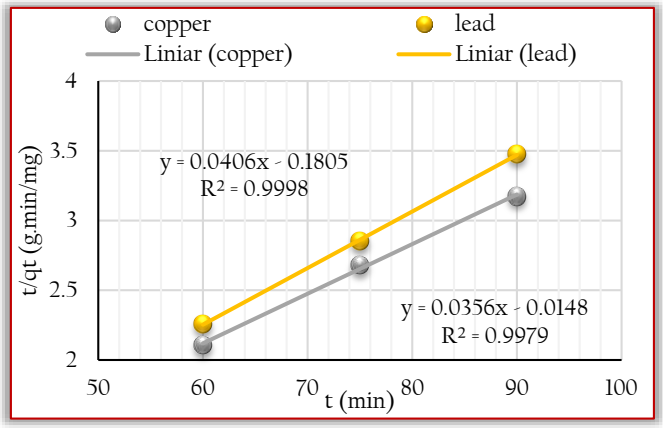

Figure 13: A plot of t/qt with time

— Elovich Model

The Elovich model applicable for chemisorption kinetics and systems in which the adsorbing surface is heterogeneous (Namasivayam and Kavitha, 2002) is given in Equation (9).

$$\frac{dq_t}{dt} = \propto e^{-\beta qt} \quad (9)$$

Integrating this equation for the boundary functions yields Equation (10).

$$q_t = \frac{1}{\beta}\ln(\propto \beta) + \frac{1}{\beta}\ln t \quad (10)$$

where α is the initial adsorption rate (mg.min/ g) and β is related to the extent of surface coverage and the activation energy for chemisorption (g mg^{-1}). A plot of qt vs. ln t in Figure 14 gives a linear trace with a slope of (1/β) and an intercept of 1/β ln (α β). The plot is linear with good correlation coefficient (R^2 = 0.0852 for copper, R^2 =0.9754 for lead).

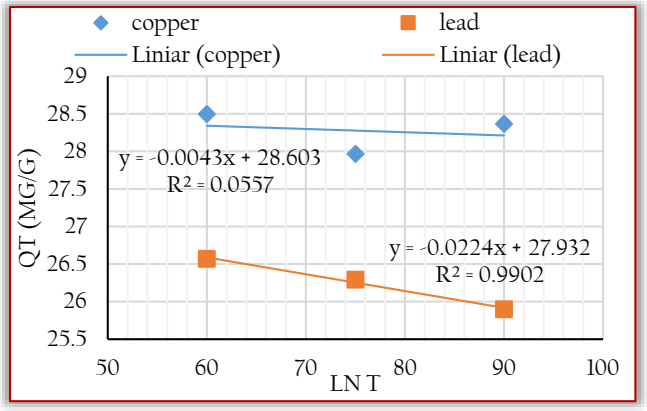

Figure 14: A plot of q_t with ln t

CONCLUSION AND RECOMMENDATIONS

Evidence provided in this study has shown that MCE have a high efficacy and have the potential to be used as an effective adsorbent for the removal of $Pb^{2+}$and Cu^{2+}ions aqueous solutions. The Langmuir isotherm model fitted the copper adsorption most with a correlation coefficient (R^2) value of 0.9992, better than for lead, while the pseudo second order kinetics fitted the lead and copper adsorption most with R^2 values of 0.9998 and 0.9979 respectively. A conclusion could be reached that pH, contact time, adsorbent weight/dose and initial metal concentration all played significant roles in the rate of adsorption of the metals. It was observed that adsorption of the metal ion was more pronounced with samples that had higher contact times. Adsorption was also higher in more basic solutions, as experimental runs with pH heading towards alkalinity showed greater adsorption capacities. This method of adsorption can be employed in purifying wastewater from metal mine effluents, metal refining and battery manufacturing facilities effluents.

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