Sorption of Pb(II) and Cu(II) by Low-Cost Magnetic Eggshells-Fe₃O₄ Powder

This study explored the feasibility of using magnetic eggshell-Fe₃O₄ powder as an adsorbent for the removal of Pb(II) and Cu(II) ions from aqueous solution. The metal ions-adsorption media interaction was characterized using XRD and FTIR. The effects of contact time, initial concentrations, temperature, solution pH and reusability of the adsorption media were investigated. The metal ions adsorption was fast and the amount of metal ions adsorbed increased with an increase in temperature, suggesting an endothermic adsorption. The kinetic data showed that the adsorption process followed the pseudo-second order kinetic model. The optimal adsorption pH value was around 5.5 at which condition the equilibrium capacity was 263.2 mg/g for Pb(II) and 250.0 mg/g for Cu(II). The adsorption equilibrium data fitted very well to the Langmuir and Freundlich adsorption isotherm models. The thermodynamics of Pb(II) and Cu(II) adsorption onto the magnetic eggshell-Fe₃O₄ powder indicated that the adsorption was spontaneous. The reusability study has proven that magnetic eggshell-Fe₃O₄ powder can be employed as a low-cost and easy to separate adsorbent.

Keywords: magnetic eggshell-Fe₃O₄, adsorption, Pb(II), Cu(II), wastewater.

Numerous heavy metal ions such as chromium, cadmium, manganese, mercury, lead and copper, among others, are known to be significantly toxic to human health and environment even at low concentrations. For instance, the uptake of lead and copper in excess doses may lead to serious kidney failure and liver disease in humans [1]. Hence, the removal of these toxic metals from wastewater has become a serious matter in the field of water pollution control. Methods for metal ions removal from aqueous solution include adsorption, chemical precipitation, solvent extraction, reverse osmosis, ion exchange, chemical oxidation and reduction, filtration and electrochemical treatment. Out of these methods, adsorption is generally preferred due to its high efficiency, availability of different adsorbents and cost effectiveness [2].

Low-cost waste bio-materials have been recognized to be very effective in dealing with industrial effluents containing heavy metals ions [3-7], and some reviews indicated that the cost of biomaterials may be negligible compared with the cost of activated carbon or ion-exchange resins [8,9]. Eggshell waste has been explored in recent years because it is economically cheap, plentiful in nature and has intrinsic pore structure [10-16]. In adsorption process, eggshell is normally applied as fine powders in industrial waste treatment. The disadvantage of this approach is the requirement of an additional costly and time-consuming separation step (filtration) to remove fine powder from solution [17,18]. Fortunately, this technical limitation can be overcome by introducing nanosized Fe₃O₄ magnetic particles onto the surface of the eggshell. The resulting media has an inherent advantage of short adsorption equilibrium time [19], convenient magnetic separation from wastewater [20] and high efficiency in treating wide concentration range (1-1000 µg mL⁻¹) of pollutants, where other techniques are ineffective, time-consuming or costly [21-24].
Consequently, in this study magnetic eggshell-Fe$_3$O$_4$ powder as adsorbent is prepared and characterized by Fourier transform infrared (FTIR), powder X-ray diffraction (XRD) and scanning electron microscope (SEM). And then the adsorbent is applied for enhanced removal of Pb(II) and Cu(II) under varying process conditions. Kinetic and equilibrium results are generated, modeled and discussed. The eggshell-Fe$_3$O$_4$ adsorbent is reusable and moreover it can be recovered easily from water with the help of an external magnet thanks to good magnetic properties.

**EXPERIMENTAL**

**Preparation of magnetic eggshells powder**

Eggshells were collected from a grocery shop in city of Pretoria, South Africa. To remove impurities and membranes, the eggshells were boiled in 1.0 mol L$^{-1}$ NaOH solution for 1 h and then rinsed several times with deionized water. Then the sample was crushed and screened through a set of sieves to get the geometrical size of 75-150 $\mu$m after being dried at 100 °C overnight.

To induce magnetic property on eggshell powder, a coprecipitation method was used. Briefly, it involved dissolving 0.04 mol of FeCl$_3$·6H$_2$O and 0.02 mol of FeCl$_2$·4H$_2$O in 50 mL of 0.5 mol L$^{-1}$ HCl solution. The resulting solution was then added dropwise to a vigorously stirred sample containing 1.5 mol L$^{-1}$ NaOH solution (250 mL) and 20 g eggshell particles (75-150 $\mu$m) at 65 °C under a nitrogen flow. Thereafter, the reaction temperature was raised to 90 °C for 0.5 h. Afterwards, the solution was continuously stirred to room temperature and the obtained magnetic eggshell powder were repeatedly washed until neutral with deionized water. Finally, the product was cooled and dried under vacuum for 12 h to obtain eggshell-Fe$_3$O$_4$ powder as adsorbent.

**Chemical reagents**

Pb(NO$_3$)$_2$ and CuSO$_4$·5H$_2$O obtained from Saarchem (Pty) Ltd., South Africa, were selected for this study as sources of Pb(II) and Cu(II) ions. The stock solutions were prepared by dissolving specified weights of Pb(NO$_3$)$_2$ and CuSO$_4$·5H$_2$O in 1000 mL of deionized water, and subsequently diluted to the required concentrations. All chemicals used in the experiments, including NaOH, FeCl$_3$·6H$_2$O, FeCl$_2$·4H$_2$O, HCl and HNO$_3$, were of analytical reagent grade and used without further purifications.

**Determination of point-of-zero charge ($pH_{pzc}$)**

The point-of-zero charge ($pH_{pzc}$) was examined to find out the surface charge of eggshell-Fe$_3$O$_4$ powder. For the determination of $pH_{pzc}$, 0.1 mol L$^{-1}$ KCl was prepared and its initial pH was adjusted between 2.0 and 12.0 by using solutions of NaOH or HCl. Then, 50 mL of 0.1 mol L$^{-1}$ KCl was taken into the reaction bottle and 0.05 g of eggshell-Fe$_3$O$_4$ powder was added to each solution. The bottles were kept for 24 h and the final pH of the solutions was measured by using a pH meter. Graphs were plotted of $pH_{initial}$ versus pH drift ($pH_{final} - pH_{initial}$) [25,26].

**Batch adsorption study**

**General procedure for adsorption of Pb$^{2+}$ and Cu$^{2+}$**

The influence of solution pH on the Pb$^{2+}$ and Cu$^{2+}$ adsorption was studied over the pH range of 4-8. The pH was adjusted using 0.1 mol L$^{-1}$ HCl or NaOH solution. In this study, 50 mL of Pb$^{2+}$ or Cu$^{2+}$ solution of 200 mg L$^{-1}$ was agitated with 0.05 g of eggshell-Fe$_3$O$_4$ powder for 24 h at 25 °C. In the subsequent investigations, experiments were performed at solution pH 5.5 to avoid any possible hydroxide precipitation.

**Kinetic studies**

Batch kinetic experiments were performed by contacting 1.0 g of eggshell-Fe$_3$O$_4$ powder in a 1.0 L batch reactor with Pb$^{2+}$ and Cu$^{2+}$ at initial concentration of 211.15 mg L$^{-1}$ and 226.6 mg L$^{-1}$, respectively. The reactor was stirred with an overhead stirrer at a speed of 280 rpm at 25 °C. 10 mL of samples were collected at different time intervals and the concentrations of Pb$^{2+}$ and Cu$^{2+}$ in the supernatant solution were analysed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) at a plasma power of 1400 W. The amount of the adsorbed metals was determined by:

$$q_t = \frac{V(c_0 - c_t)}{m}$$

where $q_t$ is the amount of metal adsorbed at any time (mg g$^{-1}$), $c_0$ (mg L$^{-1}$) is the metal ions initial concentration, $c_t$ (mg L$^{-1}$) is the metal ions concentration at any time, $V$ (L) is the volume of solution, and $m$ (g) is the weight of adsorbent.

**Equilibrium adsorption isotherm**

To generate equilibrium adsorption isotherms, Pb$^{2+}$ and Cu$^{2+}$ were contacted for 24 h at 25 °C with 0.05 g of eggshell-Fe$_3$O$_4$ powder in 50 mL solution at pH 5.5. The initial metal ions concentration ranged from 200-400 mg L$^{-1}$. At the end of the experiment, the concentrations of Pb$^{2+}$ and Cu$^{2+}$ in the supernatant solutions were determined by ICP-AES.
Reusability studies

Regeneration studies were performed using de-ionized water and low concentration solutions of NH₄Cl, NH₄OH, HCl, HNO₃, NaCl or their combination. 100 mL Pb²⁺ and Cu²⁺ solutions of 400 mg L⁻¹ metal ions concentrations were separately treated with 0.1 g eggshell-Fe₃O₄ powder for 3 h. Thereafter, the adsorbent was separated from the reaction bottles and rinsed several times with deionized water to remove excess metal ions. This was followed with the adsorbent being agitated with 200 mL of selected eluent for 3 h, filtered and dried for reuse in the next adsorption step.

Characterization methods

The structure and morphology of the eggshell, Fe₃O₄, eggshell-Fe₃O₄ powder before and after Pb(II) and Cu(II) adsorption were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM; JSM-5800LV). XRD Patterns were obtained at room temperature by a PANalytical X'Pert Pro powder diffractometer with an X'Celerator detector using Fe filtered CoKα radiation in the range of 2θ = 0-90°, and scanning rate of 0.02 s⁻¹. Fourier transform infrared spectroscopy (FTIR) spectra were recorded with a Perkin-Elmer FTIR spectrometer, using NUJOL CP as background, in the region of 800-4000 cm⁻¹, with resolution of 4 cm⁻¹.

RESULT AND DISCUSSION

Characterisation of the adsorption media

Figure 1a shows a typical XRD pattern of the Fe₃O₄ sample. The structure was identified by comparison to spectra JADE program (Materials Data XRD Pattern Processing Identification & Quantification) and matched well with some reported results [27,28]. The XRD pattern with seven characteristic peaks at 21.3, 29.2, 41.4, 50.5, 67.3 and 74.2° that correspond to (111), (220), (311), (400), (422), (511) and (440) of magnetite crystalline structure are shown in Figure 1a. Figure 1b shows the XRD spectrum of natural eggshell. The sample presented all diffraction peaks that are characteristic of calcite (CaCO₃), which is the thermodynamically most stable form of CaCO₃ with rhombohedral structure at room temperature [29]. Figures 1c-1e show the XRD patterns of eggshell-Fe₃O₄ powder before and after Pb²⁺ or Cu²⁺ adsorption. The relative phase amounts (wt.%) of Fe₃O₄ were estimated using the Rietveld method (Autoquan Program) and errors were on the 3σ level in the column to the right of the amount (inset). New peaks at 23.37, 28.89 and 29.64° observed in Figure 1d and slight change of peak intensities in Figure 1e, may suggest the possibility of Pb²⁺ and Cu²⁺ adsorption onto eggshell-Fe₃O₄ powder.

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The SEM images of eggshell and eggshell-Fe₃O₄ powder are shown in Figures 2a and 2b. As observed from Figure 2a, the eggshell powder particles consist of highly porous structure, which increased the contact area and was responsible for Fe₃O₄ loading and metal ions sorption onto eggshell powder particles [30]. After the loading of Fe₃O₄ nanoparticles (Figure 2b), surface morphology can be observed to have much asperity and are more coarsely grained, which created larger contact area and more opening sites for the metal ions to be attached. To confirm the functional groups on the adsorption media, the FTIR spectra of the samples were collected in the 800-4000 cm⁻¹ range (Figure 3). In addition to existence of Fe₃O₄ in the sample as indicated by the XRD pattern, the peak at 1075 and 3413 cm⁻¹ can be attributed to the Fe-OH and O-H stretching modes of FeOH or adsorbed wa-
ter, while the bands at 1797 cm\(^{-1}\) reflect the carbonyl group stretching [31-33]. By comparison of IR spectra of eggshell (a) and eggshell-Fe\(_3\)O\(_4\) (b), there are relative increase in peak intensities, wave number shift (\(\Delta \gamma = 36 \text{ cm}^{-1}\)) from 2922 cm\(^{-1}\) peak and the absence of 875, 1075 and 3413 cm\(^{-1}\) bands on pure eggshell. All these facts indicate a strong chemisorption of Fe\(_3\)O\(_4\) on eggshell sample [34]. It can be noted from b, c and d samples that the presence of Pb\(^{2+}\) and Cu\(^{2+}\) did not give obvious hints of chemisorption with a spectral resolution of 4 cm\(^{-1}\) in all cases, indicating that the sorption process of metal ions is physiosorption in nature.

The composite powder can be removed conveniently from water with the help of an external magnet. Figure 4a shows a digital photograph of the metal ions solution with equally dispersed eggshell-Fe\(_3\)O\(_4\) composite powder. Figure 4b shows the solution after magnetic separation using an external magnetic field. These figures demonstrate that easy, fast separation of the eggshell-Fe\(_3\)O\(_4\) composite powder can be realized in real plant operation.

**Effect of pH on Pb\(^{2+}\) and Cu\(^{2+}\) adsorption**

The relationship between pH value and adsorption capacity of Pb\(^{2+}\) and Cu\(^{2+}\) on magnetic eggshell-Fe\(_3\)O\(_4\) powder was studied and is illustrated in Figure 5. The lowest pH considered was 4 since Fe\(_3\)O\(_4\) can dissolve at pH < 4 [35]. It can be seen that the quantities of metal ions adsorbed increases with an increase in pH. Similar results were also reported for Pb\(^{2+}\) and Cu\(^{2+}\) adsorption on bulk Fe\(_3\)O\(_4\) nanosorbent [36] and on iron oxide and kaolin [37]. Such increase in adsorption can be attributed to the favorable change in surface charge and to the extent of hydrolysis of the adsorbing metal ion. As shown in the figure (inset), the surface charge becomes more negative with an increase in pH. This would enhance surface attraction of bivalent metal cations for adsorption [38-40]. It was observed during the experiments that copper was slightly precipitated when pH value of 6 was exceeded.
while at pH > 5.5 hydrolysis of Pb$^{2+}$ as polynuclear species were reported [35]. Accordingly, the subsequent experiments were done at pH 5.5 to avoid uncertainty in results as additional mechanism such as precipitation might play a role in metal removal from solution.

![Figure 4](image)

**Figure 4. Digital photograph of the metal ions solution, a) with dispersed eggshell-Fe$_3$O$_4$ powder and b) after magnetic separation using an external magnet.**

### Adsorption kinetics

The adsorption kinetics of Pb$^{2+}$ and Cu$^{2+}$ onto eggshell-Fe$_3$O$_4$ powder at 25 °C was monitored for 240 min. As seen in Figure 6, Pb$^{2+}$ was adsorbed onto eggshell-Fe$_3$O$_4$ powder rapidly in the first 60 min. After this period, the amount adsorbed did not change much with prolonged time. One reason for this could be due to the short diffusion path and high surface area of eggshell-Fe$_3$O$_4$ particles, which are favourable for the removal of ions from bulk solution onto the active sites of the solid surface. Another reason could result from the nonporous structure of Fe$_3$O$_4$ that leads only to occurrence of adsorption on the external surface. The mass transfer under these phenomena requires less time to reach equilibrium [41]. Short equilibrium time for metal ion adsorption was also reported by other researchers [42,43]. Meanwhile, the removal trend of Cu$^{2+}$ showed somewhat slower kinetics with equilibrium being reached within 180 min. The same trend was observed for adsorption of Cu$^{2+}$ on iron oxide and kaolin [37].

Further, the kinetic results were modelled using various equations and it was found that the Ho pseudo-second order model gives satisfactory description of the data. Based on equilibrium adsorption, the Ho pseudo-second-order kinetic equation is expressed as [44]:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$

(2)

and the initial sorption rate, $h_0$ (mg g$^{-1}$ min$^{-1}$) can be defined as:

$$h_0 = k_2q_e^2(t \rightarrow 0)$$

(3)

![Figure 5](image)

**Figure 5. Effect of pH on Pb$^{2+}$ and Cu$^{2+}$ adsorption on magnetic eggshell-Fe$_3$O$_4$ powder. The figure inset shows the determination of pH$_{pzc}$ of the media.**
where \( k_2 \) is the rate constant of pseudo-second-order adsorption (g/mg min). Both \( k_2 \) and \( h_0 \) could be determined experimentally by plotting of \( \frac{t}{q_t} \) against \( t \). The application of the linear form of the Ho pseudo-second-order kinetic model is presented in the inset of Figure 6. It can be seen that the kinetics of Pb\(^{2+}\) and Cu\(^{2+}\) adsorption onto eggshell-Fe\(_3\)O\(_4\) powder follow this model with correlation coefficients higher than 0.995. The calculated \( q_e \) values of Pb\(^{2+}\) and Cu\(^{2+}\) adsorption onto eggshell-Fe\(_3\)O\(_4\) powder are 239.48 and 231.64 mg g\(^{-1}\), respectively, which are close to those obtained experimentally. The constant \( k_2 \) and initial sorption rate \( h_0 \) values of Pb\(^{2+}\) and Cu\(^{2+}\) adsorption onto eggshell-Fe\(_3\)O\(_4\) powder are 5.24 \( \times 10^{-4} \) and 1.49 \( \times 10^{-4} \) g mg\(^{-1}\) min\(^{-1}\), and 30.07 and 7.84 g mg\(^{-1}\) min\(^{-1}\), respectively, suggesting the studied magnetic adsorbent would be a good adsorbent to scavenge Pb\(^{2+}\) and Cu\(^{2+}\) from contaminated water.

### Adsorption Isotherms

Many models have been proposed to explain adsorption process, among which Langmuir and Freundlich isotherms are the most used ones to describe the equilibrium sorption of metal ions [45,46]. The linear forms of the Langmuir and the Freundlich models are given by Eqs. (4) and (5), respectively:

\[
\frac{c_a}{q_e} = \frac{1}{q_m K_L} + \frac{c_a}{q_m} 
\]

\[
\log q_e = \log K_F + \frac{1}{n} \log c_e 
\]

where \( q_m \) (mg g\(^{-1}\)) is the Langmuir maximum adsorption capacity, \( K_L \) (L mg\(^{-1}\)) is the Langmuir adsorption equilibrium constant, \( K_F \) is Freundlich parameter related to adsorption capacity and \( 1/n \) is a parameter related to adsorption intensity.

The adsorption of Pb\(^{2+}\) and Cu\(^{2+}\) onto eggshell-Fe\(_3\)O\(_4\) powder at 25 °C were expressed as a relationship between the amount of adsorbate per unit of adsorbent (\( q_e \)) and equilibrium solution concentration (\( c_e \)) as shown in Figure 7. Both Pb\(^{2+}\) and Cu\(^{2+}\) adsorptions on eggshell-Fe\(_3\)O\(_4\) powder were high and increase with an increase in equilibrium concentrations and thereafter level off, suggesting that eggshell-Fe\(_3\)O\(_4\) powder has a high sorption affinity for Pb\(^{2+}\) and Cu\(^{2+}\) even at low concentrations. The adsorption data in Figures 7a and 7b fitted very well to both Langmuir and Freundlich models with correlation coefficients \( R^2 \) of 0.99 (inset). The maximum monolayer adsorption capacity (\( q_m \)) obtained for Pb\(^{2+}\) and Cu\(^{2+}\) onto eggshell-Fe\(_3\)O\(_4\) powder were 263.2 and 250.0 mg g\(^{-1}\) at 25 °C, indicating for a given temperature examined, the adsorption affinity of heavy metals is ordered as Pb\(^{2+}\) > Cu\(^{2+}\) onto eggshell-Fe\(_3\)O\(_4\) powder. The Freundlich adsorption intensity parameters (\( n \) values) were 15.87 and 16.39, also supporting the favourable adsorption of Pb\(^{2+}\) and Cu\(^{2+}\) onto eggshell-Fe\(_3\)O\(_4\) pow-
The Langmuir adsorption capacities obtained in the present study were compared with those reported in literature and are summarised in Table 1. The magnetic eggshell-Fe₃O₄ powder exhibits higher capacity than most biosorbents. These may be attributed to effect of particle size and distribution, surface structure and properties.

### Thermodynamic studies

The effect of temperature on the adsorption of Pb²⁺ and Cu²⁺ was studied in the range of 25-45 °C by using 0.05 g eggshell-Fe₃O₄ powder and 50 mL of 400 mg L⁻¹ metal ions solution. The capacity of Pb²⁺ and Cu²⁺ increased from 248.40 and 231.64 mg g⁻¹ to 267.33 and 254.14 mg g⁻¹, respectively, when the...
temperature increased from 25 to 45 °C, indicating that the adsorption was endothermic in nature. The feasibility of the adsorption process can be estimated by thermodynamic parameters of Gibbs energy change (adsGΔ), enthalpy change (adsHΔ) and entropy change (adsSΔ) by the following equations:

\[ \Delta G_{\text{ads}} = -RT \ln K_c \]  
\[ \ln K_c = \frac{\Delta S_{\text{ads}}^{\circ}}{R} - \frac{\Delta H_{\text{ads}}^{\circ}}{RT} \]  
\[ K_c = \frac{c_i}{c_e} \]

where \( K_c \) is the distribution coefficient for the adsorption, \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and \( T \) is the adsorption temperature (K). \( c_i \) and \( c_e \) are the initial and equilibrium concentration of metal ions (mg L\(^{-1}\)), respectively. \( \Delta H_{\text{ads}}^{\circ} \) and \( \Delta S_{\text{ads}}^{\circ} \) can be calculated from the slope and intercept of Eq. (7), respectively. The thermodynamic parameters at the studied temperature range are listed in Table 2. The plots of ln \( K_c \) vs. 1/T were found to be linear with a correlation coefficient \( R^2 \) = 0.95 and 0.99 for adsorption of Pb\(^{2+}\) and Cu\(^{2+}\), respectively.

As seen from Table 2, \( \Delta G_{\text{ads}} \) at all temperatures were negative and increased with an increase in temperature, indicating the feasibility and spontaneity of the adsorption of Pb\(^{2+}\) and Cu\(^{2+}\) onto eggshell-Fe\(_3\)O\(_4\) powder. The positive value of \( \Delta H_{\text{ads}} \) confirmed the endothermic nature of the adsorption process, while the positive value of \( \Delta S_{\text{ads}}^{\circ} \) revealed the increase in randomness at the solid/solution interface during the adsorption process [58]. This increase resulted from the extra translational entropy gained by the water molecules previously adsorbed onto sorbent but displaced by Pb\(^{2+}\) and Cu\(^{2+}\). According to Seti et al. [59] and Yu et al. [60], \( \Delta G_{\text{ads}} \) values between -20 and 0 kJ/mol correspond to spontaneous physical process, while that with values between -80 and -400 kJ/mol corresponds to chemisorption. From the \( \Delta G_{\text{ads}} \) values obtained in this study, it can be deduced that the adsorption onto eggshell-Fe\(_3\)O\(_4\) powder is dominated

### Table 1. Comparison of sorption capacities of adsorbents

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>Metal</th>
<th>Conditions</th>
<th>( q_m ) / mg g(^{-1})</th>
<th>Reference</th>
</tr>
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<tr>
<td>Eggshell</td>
<td>Cu(II)</td>
<td>-</td>
<td>5.03</td>
<td>[11]</td>
</tr>
<tr>
<td>Calcined eggshell powder</td>
<td>Pb(II)</td>
<td>pH 5.5, ( T = 298 K )</td>
<td>343.3</td>
<td>[14]</td>
</tr>
<tr>
<td>Iron oxide</td>
<td>Pb(II)</td>
<td>pH 5.5, ( T = 298 K )</td>
<td>36</td>
<td>[27]</td>
</tr>
<tr>
<td>Chitosan/magnetite composite powder</td>
<td>Pb(II)</td>
<td>pH 6.0, ( T = 298 K )</td>
<td>63.33</td>
<td>[28]</td>
</tr>
<tr>
<td>Zeolite</td>
<td>Pb(II)</td>
<td>pH 5.0, ( T = 298 K )</td>
<td>123</td>
<td>[47]</td>
</tr>
<tr>
<td>Magnetic-poly-2-acrylamido-2-methyl-1-propansulfonic acid p(AMPS) hydrogels</td>
<td>Pb(II)</td>
<td>-</td>
<td>140.84</td>
<td>[48]</td>
</tr>
<tr>
<td>Nano-alumina modified with 2,4-dinitrophenylhydrazine</td>
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<td>[49]</td>
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<tr>
<td>Nano mesoporous silica</td>
<td>Pb(II)</td>
<td>-</td>
<td>57.74</td>
<td>[50]</td>
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<tr>
<td>Magnetic Fe(_3)O(_4) yeast</td>
<td>Pb(II)</td>
<td>-</td>
<td>89.29</td>
<td>[51]</td>
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<td>Azolla filicaloides</td>
<td>Pb(II)</td>
<td>-</td>
<td>228</td>
<td>[52]</td>
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<td>pH 6.0</td>
<td>142.9</td>
<td>[53]</td>
</tr>
<tr>
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<td>Cu(II)</td>
<td>-</td>
<td>133.3</td>
<td>[54]</td>
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<td>[56]</td>
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<td>This study</td>
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### Table 2. Estimated values of \( \Delta G_{\text{ads}} \), \( \Delta H_{\text{ads}} \) and \( \Delta S_{\text{ads}}^{\circ} \) for the adsorption of Pb(II) and Cu(II) onto eggshell-Fe\(_3\)O\(_4\) powder at different temperatures; pH 5.5, amount of adsorbent: 1.0 g/L

<table>
<thead>
<tr>
<th>( c_0 ) / mg L(^{-1})</th>
<th>( T ) / K</th>
<th>( \Delta G_{\text{ads}}^{\circ} ) / kJ mol(^{-1})</th>
<th>( \Delta H_{\text{ads}}^{\circ} ) / kJ mol(^{-1})</th>
<th>( \Delta S_{\text{ads}}^{\circ} ) / J mol(^{-1}) K(^{-1})</th>
<th>( R^2 )</th>
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<tr>
<td>400 (Pb(^{2+}))</td>
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<td>20.55</td>
<td>0.95</td>
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<td></td>
<td>318</td>
<td>-1.85</td>
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<td></td>
</tr>
<tr>
<td>400 (Cu(^{2+}))</td>
<td>298</td>
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<td>11.13</td>
<td>0.99</td>
</tr>
<tr>
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<td>318</td>
<td>-1.15</td>
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</table>
by physiosorption, which matches the indication from the FTIR spectra.

Reusability studies

Desorption of Pb$^{2+}$ and Cu$^{2+}$ can be achieved at low pH due to the pH-dependent adsorption on magnetic eggshell-Fe$_3$O$_4$ powder. To find the most potential eluent for the desorption of Pb$^{2+}$ and Cu$^{2+}$ and on the basis of cheap, effective, non-polluting and minimum damage to the adsorbent, several eluents (deionized water, NH$_4$Cl, NH$_4$OH, HCl, HNO$_3$ and NaCl) or combination were screened for their potential to desorb Pb$^{2+}$ and Cu$^{2+}$ from metal-loaded eggshell-Fe$_3$O$_4$ powder. The desorption efficiency of HNO$_3$ solution (pH 3.5) was found to be the most effective eluent for the desorption process. The adsorption capacities of eggshell-Fe$_3$O$_4$ composite powder for adsorption-desorption cycles are illustrated in Figure 8.

**Figure 8.** Reusability studies of eggshell-Fe$_3$O$_4$ composite powder.

Adsorption was performed at 25 °C, using 50 mL solutions Pb$^{2+}$ and Cu$^{2+}$ of initial concentration of 400 mg L$^{-1}$ at pH 5.5.

It is noteworthy that the used eggshell-Fe$_3$O$_4$ powder after desorption can maintain an adsorption capacity of both Pb$^{2+}$ and Cu$^{2+}$ above 150 mg g$^{-1}$ after 5 cycles. The capacity loss might be due to the loss of some active sites on eggshell-Fe$_3$O$_4$ powder after treatment with HNO$_3$ eluent. Compared to the commercially available adsorbent such as activated carbons, whose regeneration accounts for about 75% of the total operating and maintenance costs [61], eggshell-Fe$_3$O$_4$ powder is a cost-effective with high adsorption capacity.

CONCLUSION

In this study, magnetic eggshell-Fe$_3$O$_4$ powder was prepared using a simple coprecipitation method and employed as an adsorbent for the removal of Pb$^{2+}$ and Cu$^{2+}$ from aqueous solutions. The material showed enhanced Pb$^{2+}$ and Cu$^{2+}$ adsorption capacities compared with most materials reported in literature. The equilibrium data followed both the Langmuir and Freundlich isotherm models. The maximum adsorption capacities of 248.4 and 231.64 mg g$^{-1}$ for Pb(II) and Cu(II) occurred at pH 5.5 and 25 °C. These results permit us to conclude that eggshell-Fe$_3$O$_4$ powder is a promising low-cost and high-efficiency adsorbent for Pb$^{2+}$ and Cu$^{2+}$ removal from wastewater and can be applied in a magnetically-assisted water treatment technology.

Acknowledgement

The authors acknowledge the Tshwane University of Technology for the support and funds provided for the completion of this work.

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SORPCIJA Pb(II) I Cu(II) NA JEFTINOM MAGNETNOM PRAHU LJUSKI JAJETA I Fe3O4

U radu je ispitivana primenamagnetnog praha ljuske jajeta i Fe3O4 kao adsorbenta za uklanjanje Pb(II) i Cu(II) jona iz vodenih rastvora. Interakcija metalnih jona i adsorbenta okarakterisana je primenom XRD i FTIR. Ispitivan je uticaj kontaktog vremena, početnih koncentracija, temperature, pH rastvora i mogućnost ponovne upotrebe adsorbenta. Adsorpcija metalnih jona bila je brza, a količina adsorbovanih jona povećavala se sa porastom temperature, ukazujući na endotermnu adsorpciju. Kinetički podaci pokazali su da proces adsorpcije prati model kinetike pseudo-drugog reda. Optimalna pH vrednost adsorpcije bila je oko 5,5, pri čemu je ravnovesni kapacitet iznosio 263,2 mg/g za Pb(II) i 250,0 za Cu(II). Ravnovesni podaci se dobro slažu sa Langmuir-ovim i Freundlich-ovim modelom izoterme. Termodinamika adsorpcije Pb(II) i Cu(II) na magnetni prah ljuske jajeta i Fe3O4 ukazala je na spontanu adsorpciju. Studija o ponovnoj primenljivosti dokazala je da se magnetni prah ljuske jajeta i Fe3O4 može koristiti kao jeftini adsorbent koji se lako separe.

Ključne reči: magnetni prah ljuske jajeta i Fe3O4, adsorpcija, Pb(II), Cu(II), otpadna voda.