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Co-Adsorption of Pb (II) and Cu(II) ions onto Bentonite-Chitosan Composites: Equilibrium Isotherm Modelling and Desorption Studies

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ABSTRACT

Lead (Pb) and copper (Cu) ions are frequently encountered together in drinking water and wastewater. Adsorption with the use of composite materials made from bentonite clays and biodegradable polymers seems to be a promising cost-effective technique for the removal of heavy metals from water. This study investigated the co-adsorption of Pb(II) and Cu(II) ions onto Bentonite-Chitosan (Bt-Ch) composites from binary aqueous solutions using batch procedure. The experimental adsorption data from equilibrium studies were subjected to various single- and multi-component equilibrium isotherm equations for the best fits, and the obtained parameters were compared. The multi-component non-modified Langmuir model predicted Q_{max} values for both Pb(II) and Cu(II) ions in the binary system that were quite similar to those obtained from the single-component Langmuir model. The Q_{max} values obtained from the single-component Langmuir model for Pb(II) ions were about 60% higher than those obtained for Cu(II) ions. Desorption studies (even though subsequent adsorption efficiency decreases after the second cycle) demonstrated that Bt-Ch composites exhibited good potential for re-use after five cycles of regeneration, thus, indicating their potential as an effective adsorbent for simultaneous removal of Pb (II) and Cu (II) ions from water sources.

Keywords: Bentonite-Chitosan composites, Co-adsorption, Pb(II) adsorption, Cu(II) adsorption, Desorption, Isotherm Modelling.

INTRODUCTION

The presence of multiple heavy metals in various water sources above recommended limits continues to be a growing public concern due to potential health risks. Among the metal ions that still draw significant attention are lead (Pb) and copper (Cu) ions [1]. The major source of Pb contamination in water often arises from industrial effluents, particularly from the manufacturing of lead-acid batteries (and electrodes) [2,3]. Mining activities also contribute to Pb pollution; for example, artisanal gold mining in rural communities of Zamfara, Nigeria, has led to severe Pb contamination of water sources, resulting in widespread poisoning and even fatalities [4–6]. Cu, on the other hand, is a very common metal ion that occurs naturally in the environment through various phenomena and widely used in electrical industries, fungicides, and anti-fouling paints [7]. Although Cu is an essential trace element,

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excessive exposure to high levels of Cu can be fatal.

Among all the available methods, adsorption has been reported as a cost-effective technique for the removal of toxic metals from water, especially when using naturally derived materials such as chitosan biopolymers and bentonite clay[8]. Numerous studies in the literature focus on single-component adsorption of heavy metal ions, including Pb and Cu. However, since water sources usually contain multiple metals above permissible limits, there is a need for the simultaneous removal of two metals in binary component systems. Pb(II) and Cu(II) ions exhibit strong affinities for the amine ($–NH_2$) and hydroxyl (–OH) groups of chitosan, which are present in composites or beads [9]. This was demonstrated in our previous study, which examined the effect of competing ions on Pb(II) adsorption from a multi-component solution [10]. Although a few studies have reported simultaneous adsorption of Pb and Cu (or each of these metals in combination with other heavy metals) from multi- or binary-component solutions, they often rely on single-component equilibrium isotherm equations to optimise adsorption parameters, ignoring the competitive interactions among adsorbates, which are essential for accurately predicting contaminant migration and adsorbent performance [1,11,12].

Therefore, the present study aims to investigate the co-adsorption of Pb(II) and Cu(II) ions onto Bt-Ch composites and beads in binary metal systems. An adsorption study was previously performed using surface response-optimal designs to examine how several factors affect Pb-Cu adsorption. The results showed that the adsorption capacity (mg/g) was influenced by pH, adsorbent dosage, and initial concentration, but was independent of contact time [8]. For this reason, kinetic investigations were omitted in this current study, as the adsorption was not affected by contact time. The experimental adsorption data obtained from equilibrium studies were analysed using both multi- and single-component equilibrium isotherm equations to identify the best fits, and the obtained parameters were compared. A non-linear modelling method was employed to analyse the adsorption equilibrium process and optimisation was done using the "Solver add-in" in Excel Microsoft 365. In addition, the desorption experiments were conducted to access the reusability of Bt-Ch composites for the co-adsorption of Pb(II) and Cu(II) ions from binary solutions.

MATERIALS AND METHODS

Starting materials

The bentonite, Cloisite® Na+, was obtained from Rockwood Additives (now BYK Limited) and used as the layered silicate

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starting material. Chitosan biopolymer (190,000–310,000 medium molecular weight; 75-85% deacetylated), lead (II) nitrate (≥ 99.95%), copper (II) nitrate hydrate (≥ 99.95%), sodium hydroxide (reagent grade, 97%, pellets), Ethylenediaminetetraacetic acid (EDTA; disodium salt), and the stock standard solutions (for ICP) of Pb (II) and Cu (II) were obtained from Merck, UK. Sodium hydroxide (reagent grade, 97%, pellets) and nitric acid (5%) were used to prepare aqueous basic and acidic solutions, respectively. All chemicals used, unless otherwise stated, were of analytical grade purity and preparations were made using deionised water.

Adsorbent preparation

The Bt-Ch composites, prepared by combining bentonite clay and chitosan biopolymer in a 70/30 weight ratio using the solution blending method (as reported in detail in our previous study), were used as an adsorbent. The preparation and characterisation of this adsorbent have previously been reported in detail [8,10].

Batch adsorption experiments

To prepare the stock solutions (1000 mg/L) of Pb(II) and Cu(II) ions, 1.599 g of lead(II) nitrate and 3.235 g of copper (II) nitrate were dissolved in ultrapure deionised water. The resulting solutions were then preserved with the addition of 10 mL of a 5% w/v aqueous HNO_3 solution. Aqueous binary working solutions of Pb (II) and Cu (II) were prepared daily. This involved accurately measuring the required volumes of the Pb (II) and Cu (II) stock solutions into a clean volumetric flask, followed by dilution with ultrapure deionised water to achieve the desired final volume and initial concentrations for the co-adsorption experiments. The resulting binary solution was then mixed thoroughly to ensure homogeneity.

Adsorption experiments were performed at the Materials and Engineering Research Institute (MERI), Sheffield Hallam University, UK, following the methodology outlined in our previous study[8]. It was conducted in cleaned and sterilised Nalgene centrifuge plastic tubes (50 mL capacity). The centrifuge plastic bottles together with their contents were agitated using a Gyratory Water Bath shaker (Model G76D; New Brunswick Scientific, Edison. N.J. U.S.A). After specified times, the mixtures were centrifuged (using a Sorvall RC6 Superspeed Centrifuge) at 3000 rpm for 5 min and the supernatant collected and stored in cleaned and sterilised Fisher-brand PP centrifuge tubes (15 mL capacity) that were appropriately labelled for analysis of Pb and Cu ions.

During this sorption experiment, careful consideration was looked into as these metals can easily precipitates at higher pH

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levels to form their respective hydroxides. For instance, the Cu(II) ion, also known as the cupric ion, is soluble and exists as a free form particularly in low pH conditions (generally below pH 6), and above the pH of 6.0, it precipitates readily as copper hydroxide [13]. Similar chemistry was observed for Pb ions as indicated in previous studies [8,10,14]. Therefore, the adsorption experiments were carried out at pH of less than 6 to ensure Pb and Cu ions are removed just by adsorption processes without the effect of precipitation. In this study, the effect of pH was examined by varying the pH value from 2 to 6.

Simultaneous quantitative measurements of Pb(II) and Cu(II) ions were performed at the Biomolecular Sciences Research Centre (BMRC), Sheffield Hallam University, UK, using an Agilent 5110 ICP-OES instrument at wavelengths of 220.353 nm and 327.395 nm, respectively. The operating conditions of the ICP-OES instrument were the same as described in our earlier work [8]. This procedure was followed during the desorption experiments.

The amount Pb(II) and Cu(II) ions per unit mass of Bt-Ch composites (adsorbents) and percent adsorption performance (%) were calculated using equations 1 and 2, respectively.

$$q_e = \frac{C_i - C_f}{M} \times V \quad (1)$$

$$\% \text{ Adsorption} = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

Where q_e (mg Pb(II) or Cu(II) ions g^{-1} Bt-Ch composites) is the adsorption capacity, and C_i and C_f (mg L^{-1}) are the initial and final concentrations of the Pb (II) or Cu(II) ions before and after the adsorption experiment, respectively. V(L) is the volume of solutions and M (g) is the mass of the Bt-Ch composites (adsorbent).

Adsorption equilibrium study and Isotherm modelling

In this study, the adsorption equilibrium experiment was conducted using a wider range of initial concentrations (10 to 500 mg L^{-1}) of binary aqueous solutions containing Pb(II) and Cu(II) ions. This experiment was performed based on the optimal experimental conditions obtained from the surface response-optimal designs of our previous study[8]. Thus, 0.05 g of each adsorbent was exposed to 25 mL of binary solutions containing Pb(II) and Cu(II) ions with varying concentrations (as stated above) at pH 4.5, agitation time of 60 minutes (with the speed of 230 rpm) and at room temperature (25°C). The equilibrium adsorption capacities, qe (mg/g) were calculated and then plotted against the corresponding respective equilibrium concentrations, Ce (mg/L) for adsorption

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isotherm modelling. The experimental adsorption data from equilibrium studies were subjected to various single- and multi-component Langmuir and Freundlich isotherm equations for the best fits, and the obtained parameters were compared.

The non-linear single-component Langmuir and Freundlich equations, along with the multi-component isotherms (non-modified Langmuir, modified Langmuir, and extended Freundlich models), are presented and reported in our previous study [8].

If the experimental data is adequately described by the Langmuir model (single-component system), the R_L value (separation factor) can be calculated from the expression given below.

$$R_L = \frac{1}{1+K_L C_o} \quad (3)$$

Where, K_L is the Langmuir equilibrium constant, and C_o (mg/L) is the initial adsorbate concentration. R_L value indicates the adsorption nature to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The correlation coefficient (R^2) and nonlinear chi-square test (χ^2) were used to evaluate the goodness of fit for single-component isotherm modelling. In addition to correlation coefficient (R^2), the Marquardt's percent standard deviation (MPSD) was used to identify the best-fit of the multi-component isotherm model.

Desorption studies

The preliminary desorption experiments for each metal (single adsorption of Pb and Cu) using aqueous HCl and EDTA showed that Pb was well recovered with both HCl and EDTA, whereas Cu was recovered only with EDTA and very poorly with HCl. Since this study involved adsorption of binary Pb-Cu solutions, it was anticipated that dilute EDTA solutions would be more effective for simultaneously desorbing Pb and Cu ions from Bt-Ch composites, as both metals have a strong affinity for the chelating agent EDTA [8,15]. Therefore, dilute aqueous EDTA solution was used as the stripping (desorbing) agent to simultaneously recover both Pb and Cu ions adsorbed onto Bt-Ch composites.

The batch desorption procedure as described in our earlier work was used [10]. It was carried out after exposing 0.2 g of each adsorbent to 100 mg/L Pb-Cu binary solutions (25 ml; pH 4.5; agitation time = 10 minutes). After assessing the amounts of Pb and Cu ions adsorbed, the loaded adsorbents were agitated with 25 mL 0.01 M EDTA solutions for 120 minutes and filtered for recovered Pb(II) and Cu(II) ions analysis. The treated adsorbents (with EDTA to remove Pb and Cu) were stabilised and washed with 25 ml of de-ionised water (3

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times) prior to re-use. The adsorption-desorption cycles were repeated 5 times to explore the reusability of Bt-Ch composites. The percent desorption (%) was calculated using equation 4 [10,16].

$$\% \text{ Desorption} = \frac{C_d V_d}{M q_e} \times 100 \quad (4)$$

Where C_d (mg/L) is the concentration of Pb(II) and Cu(II) ions desorbed from Bt-Ch composites, V_d (L) is the volume of desorbed solution, M (g) is the mass of adsorbent (Bt-Ch composites), and q_e (mg/g) is the adsorption capacity of Bt-Ch composites for Pb(II) and Cu(II) ions.

RESULT AND DISCUSSION

Adsorption equilibrium isotherm studies

The equilibrium adsorption data for the simultaneous uptake of Pb(II) and Cu(II) were fitted and analysed using a range of non-linear single- and multi-component isotherm models. For single-component isotherms, both Langmuir and Freundlich equations were used. However, non-modified Langmuir, modified Langmuir and extended Freundlich model equations were further employed for multi-component isotherm modelling. Figure 1 presents the single- and multi-component isotherms models for co-adsorption of Pb(II)-Cu(II) onto Bt-Ch composites, while the corresponding constants (and calculated values) derived from these equations are summarised in Table 1.

Single-component Isotherm modelling

Generally, the equilibrium data obtained from co-adsorption of Pb(II)-Cu(II) ions (onto Bt-Ch composites) correlated well with both Langmuir and Freundlich isotherms studied (correlation coefficient, R^2 = 0.999) In addition, the chi-square (X^2) values obtained were quite similar, indicating that under these experimental conditions, both monolayer and heterogeneous adsorption processes may coexist. This is consistent with the earlier adsorption isotherm studies of Pb (II) ions in a single-metal system, as reported in our previous study[10]. However, the Q_{max} values (based on the Langmuir isotherm) obtained in this binary study were approximately two-times lower than the Q_{max} values reported in the earlier single-Pb study for Bt-Ch composites[8,10]. This result demonstrates that Cu(II) ions compete with Pb(II) ions for the available adsorption sites (on the Bt-Ch composites) and reduces Pb(II)-loadings significantly. This is similar to the previous binary adsorption study carried out by Ngah and Fatinathan (2010), which showed that the Pb uptake (mg/g) by chitosan-triphosphate beads in a binary metal system (Pb-Cu) was three times lower compared to the value obtained by the same adsorbent in a single metal system [9].

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In terms of adsorbent performance, the Qmax values obtained for the co-adsorption of Pb(II) and Cu(II) ions onto Bt-Ch composites were 18.26 ± 1.73 mg/g and 12.15 ± 0.51 mg/g, respectively. The higher uptake of Pb ions indicates that Bt-Ch composites exhibit a stronger affinity toward Pb, which can be attributed to the greater contribution of clay adsorption sites, given the lower chitosan content as evidenced by thermogravimetric analysis (TGA) results from our earlier characterisation study[10]. However, this finding contrasts with our previous adsorption study using a similar adsorbent in beads-form (with the same composite ratio), where a stronger affinity toward Cu was observed during competitive adsorption, reflected in higher Q_{max} values compared to Pb uptake. This difference arises because the beads contain more chitosan, as confirmed by TGA results from the earlier characterisation study, providing additional active sites through the chitosan biopolymer, and that Cu forms the most stable complexes among transition metals with glucosamine, the monomer unit of chitosan, which explains the higher Cu ion loading observed in Bt-Ch beads [8,10].

In this study, the calculated separation factor (RL) values were found to be below 1.0 for both Pb(II) and Cu(II) ions, indicating that the simultaneous adsorption of Pb(II) and Cu(II) onto Bt-Ch composites is favorable under the present experimental conditions.

From the Freundlich isotherms, the estimated Freundlich constant (K_F) values obtained (in this study, binary-metal system) for Pb(II) ions by Bt-Ch composites was 8.88 ± 1.39. This value was much lower compared to the K_F values obtained from our previous adsorption study of single-metal system for Pb(II) ions by Bt-Ch composites [10]. The values of K_F obtained for Pb(II) ions were slightly higher compared to values obtained for Cu (II) ions (i.e., 7.22 ± 0.31) regarding the binary adsorption by Bt-Ch composites. The Freundlich constant (K_F) characterises the strength of the adsorption, and a higher K_F value indicates that higher loading of adsorbate (such as metal ions) onto adsorbent could be achieved [17]. This explains the higher Q_{max} values obtained for Pb (18.26 ± 1.73 mg/g) compared to the amount obtained for Cu (12.15 ± 0.51 mg/g). This contrasts with the previous study carried out by Ngah and Fatinathan (2010), which showed that the K_F values obtained for Cu(II) ions were higher compared to the values obtained for Pb(II) ions during binary adsorption by chitosan-triphosphate beads [1]. The n value known as Freundlich exponent, was generally very low for both Pb (II) and Cu(II) ions regarding the two adsorbents studied. The observed n values fall within the range of 0 to 1, and since it is closer to zero, this implies that the surfaces

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of these adsorbents in contact with Pb(II) and Cu(II) ions are heterogeneous, a value below unity also usually suggests a chemisorption process [18].

Multi-component Isotherm modelling

The equilibrium adsorption data from simultaneous adsorption of Pb(II) and Cu(II) ions (onto Bt-Ch composites) were also fitted using three different multi-component isotherm models as shown in Figure 1, and the all the calculated parameters are summarised in Table 1. Based on the correlation coefficients ($R^2 = 0.999$), the co-adsorption of Pb(II)-Cu(II) ions onto Bt-Ch composites correlated well with non-modified Langmuir, modified Langmuir and extended Freundlich isotherm models. In addition, Marquardt's percent standard deviation (MPSD) was further employed to access the quality of the fits concerning multi-component isotherm modelling of binary adsorption of Pb(II)-Cu(II) onto Bt-Ch composites. High MPSD values (e.g., close to 100) indicate high bias between the experimental data and the model [19]. In this study, the MPSD value obtained were generally low (i.e., below 25), showing a good fit to the experimental data.

The multi-component non-modified Langmuir model predicted quite similar Q_{max} values for both Pb(II) and Cu(II) ions (in the binary metal system) as compared to the Q_{max} values derived from the single-component Langmuir model for the binary adsorption system (Table 1). Even though the Langmuir constants ($K_{L,i}$) obtained from the multi-component non-modified Langmuir model differs slightly (with respect to the values obtained from single-component Langmuir model), the model could describe the behaviours of the simultaneous adsorption of Pb(II) and Cu(II) ions in binary solutions by Bt-Ch composites.

Concerning the multi-component modified Langmuir model, the Q_{max} value predicted from the modified Langmuir model in respect to Cu(II) ions were also similar to the values obtained from the corresponding single-component Langmuir model. However, the Q_{max} values for adsorption of Pb(II) onto Bt-Ch composites were higher compared to the values predicted by the single-component Langmuir and multi-component non-modified Langmuir models. The introduction of the interaction term ($\eta_{L,i}$) as per the modified Langmuir model may only have little influence on the model, since the $\eta_{L,i}$ values estimated were less than 1.0, and therefore, the parameters obtained from the modified Langmuir model are less reliable compared to those obtained from non-modified Langmuir. It has been suggested that when the estimated $\eta_{L,i}$ value is much greater than 1.0, the parameters obtained from modified Langmuir model should be used (instead of those obtained from non-modified Langmuir) to predict the

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binary-system adsorption [20]. Overall, the resulted slight deviance and overestimation of Pb(II) ions loadings by Bt-Ch composites, may be due to some complexities resulted from the shortcoming of this model.

Like the single-component Freundlich model, the multi-component Freundlich isotherm model fitted well regarding the simultaneous adsorption of Pb(II) and Cu(II) ions assuming multilayer coverage and heterogeneous surface sites of Bt-Ch composite. Although the obtained values of Freundlich constant (Kf,i) and Freundlich exponent (n,i) were slightly different from those obtained from the single- component Freundlich model.

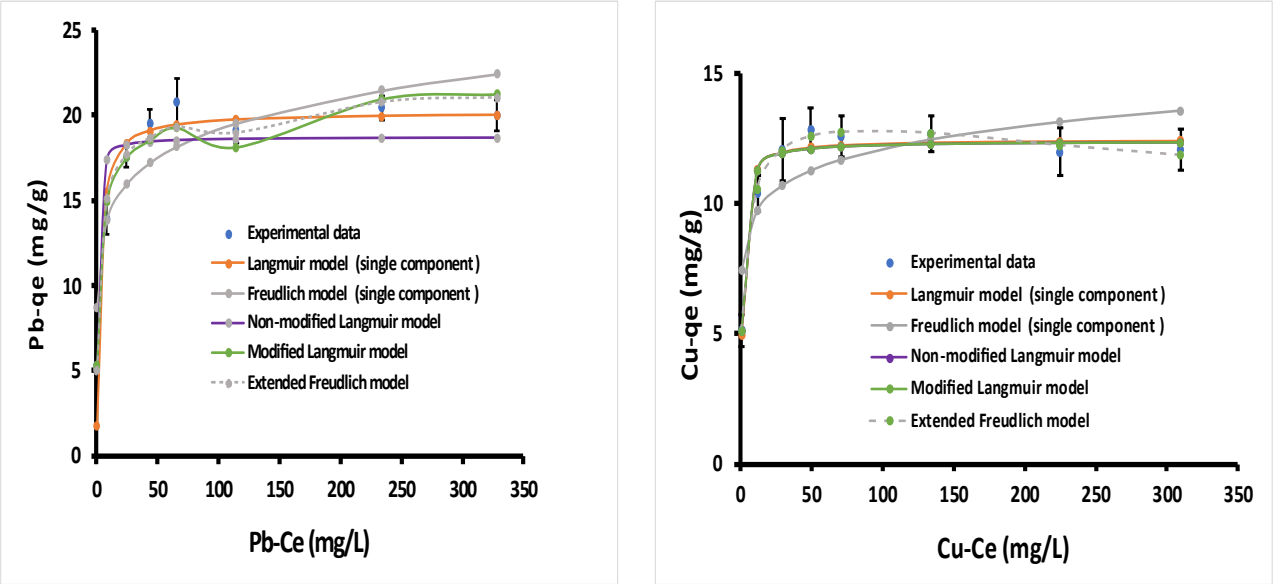


Figure 1: The non-linear single- and multi-component isotherms for co-adsorption of Pb(II)-Cu(II) onto Bt-Ch composites.

Note: at 25 ^{O}C. pH = 4.5; adsorbent amount = 0.05 g; agitation time (at 230 rpm) = 60 minutes; Initial concentrations of Pb(II) and Cu(II) ions in binary solution = 10 - 350 mg/L; Each data-point represents mean ± standard deviation of three (3) different experiments (n = 3).

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Table 1: The fitting parameters of Single-component and multi-component isotherms for the co-adsorption of Pb(II)-Cu(II) onto Bt-Ch composites

Single-component Isotherm Models	Bt-Ch composites	
	Pb	Cu
Langmuir		
Q_{max}	18.26 ± 1.73	12.15 ± 0.51
K_L	0.280 ± 0.12	1.004 ± 0.20
R_L	0.010–0.263	0.003–0.091
R^2	0.999 ± 0.00	0.999 ± 0.00
X^2	0.188 ± 0.06	0.045 ± 0.02
Freundlich		
K_F	8.883 ± 1.39	7.223 ± 0.31
n	0.143 ± 0.01	0.109 ± 0.01
R^2	0.999 ± 0.00	0.999 ± 0.00
X^2	0.206 ± 0.05	0.119 ± 0.05
Multi-component Isotherm Models	Bt-Ch composites	
	Pb (i =1)	Cu (i =2)
Non-modified Langmuir		
$q_{m,i}$	16.36 ± 2.07	11.99 ± 0.51
$K_{L,i}$	1.55 ± 1.02	1.126 ± 0.25
R^2	0.999 ± 0.00	0.999 ± 0.00
MPSD	15.56 ± 4.60	8.025 ± 2.57
Modified Langmuir		
$q_{m,i}$	65.92 ± 22.7	11.99 ± 0.51
$K_{L,i}$	0.224 ± 0.19	0.680 ± 0.07
$\eta_{L,i}$	0.649 ± 0.46	0.616 ± 0.08
R^2	0.999 ± 0.00	0.999 ± 0.00
MPSD	8.694 ± 2.32	10.36 ± 3.32
Extended Freundlich		
$K_{f,i}$	13.85 ± 10.3	5.498 ± 0.19
$n_{,i}$	0.115 ± 0.12	0.332 ± 0.12
$x_{,i}$	2.794 ± 2.78	0.053 ± 0.05
$y_{,i}$	0.204 ± 0.25	0.054 ± 0.05
$z_{,i}$	1.342 ± 1.12	0.913 ± 0.31
R^2	0.999 ± 0.00	0.999 ± 0.00
MPSD	9.354 ± 4.46	6.640 ± 5.01

Note: q_m and $q_{m,I}$ are monolayer adsorption capacity for single and i component (mg/g); K_L and $K_{L,I}$ are the Langmuir constants for single and i component, respectively (L/mg); R_L is the separation constant (dimensionless); $\eta_{L,i}$ is the interaction factor for modified Langmuir equation; K_F and $K_{f,I}$ are the Freundlich constants for single and i component, respectively (L/g), n and $n_{,i}$ are the Freundlich exponents for single and i component, respectively (unitless-ranging from 0 to 1); $x_{,I}$, $y_{,I}$, and $z_{,I}$ are the parameters of extended Freundlich model for i component; R^2 is the coefficient of correlation; X^2 is the nonlinear chi-square; and MPSD is an abbreviation for Marquardt's percent standard deviation used for minimising of error in nonlinear modelling. Each value represents mean ± standard deviation of three (3) different samples (n = 3). R_L values are range between the lowest and highest value, and were calculated based on K_L and initial Pb(II)/Cu(II) concentration, (C_O) ranging from 10 – 500 mg/L

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Desorption studies

The results for the desorption (recovery) of adsorbed Pb(II) and Cu(II) ions using different EDTA concentrations from our previous study showed that the optimal recovery of both ions was achieved with 0.01 mol/L EDTA aqueous solutions. Accordingly, this concentration of EDTA (0.01 mol/L) was used in the present study for the desorption of adsorbed Pb(II) and Cu(II) ions from the Bt-Ch composites.

The adsorption and desorption percentages of both Pb(II) and Cu(II) ions recovered from Bt-Ch composites are shown in Figure 2. As observed, about 80% and 60% adsorption was achieved in the first cycle for Pb(II) and Cu(II), respectively, while the desorption percentages for both metal ions in the first cycle were about 90%. In the second cycle, the adsorption of both metal ions was similar to the percentages obtained in the first cycle; however, there was a significant reduction in desorption percentages (about 60%) for both metal ions. There is no clear explanation for this decrease, but we anticipate that it might be due to measurement issues from ICP-OES. For subsequent adsorption-desorption cycles (third to fifth), the adsorption percentages for both Pb and Cu ions decreased significantly, whereas the desorption percentages remained similar to the values obtained in the first cycle, maintaining a constant level of about 90%. However, this contrasts with our previous adsorption-desorption study using a similar adsorbent in bead form (with the same composite ratio), where serial adsorption-desorption steps were conducted up to five times, and the observed percentages for both adsorption and desorption of Pb(II) and Cu(II) remained similar to those obtained in the initial cycle[8]. This indicates that the adsorbent (Bt-Ch composite) was less stable (compared to its bead counterpart), with possible losses of chitosan during successive adsorption-desorption cycles, leading to an apparent decline in adsorption efficiency after second cycle. Overall, the results indicated that the Bt-Ch composites exhibited good reusability for the simultaneous removal of both Pb(II) and Cu(II) ions and portrayed good recoveries.

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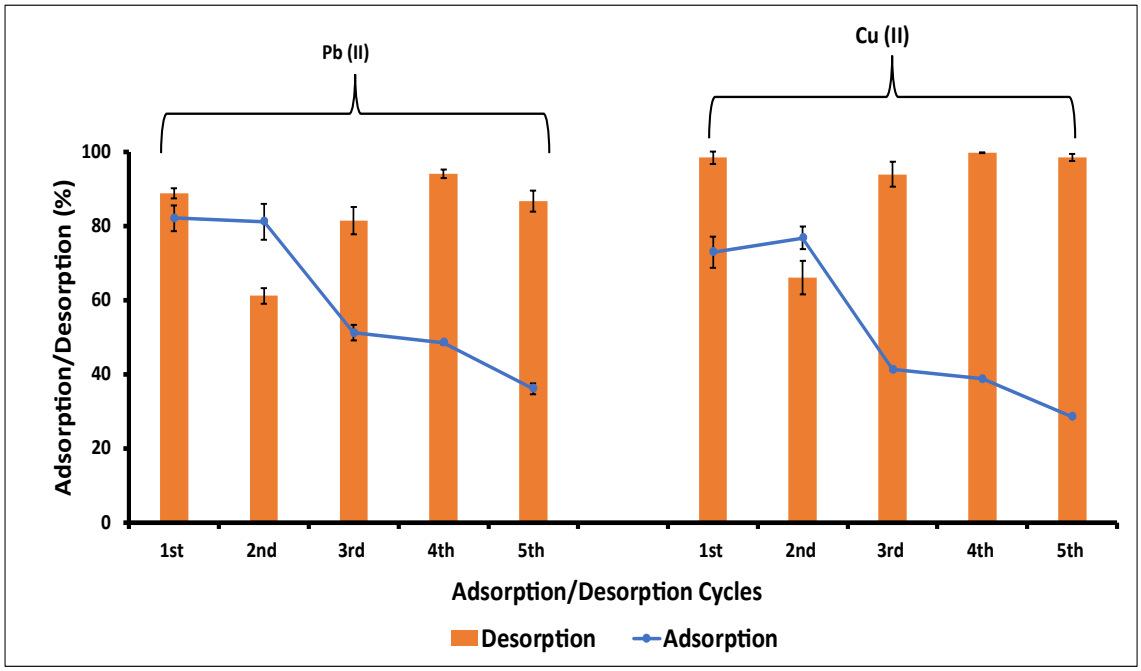


Figure 2: Charts showing the serial % Adsorption/Desorption of Pb (II) and Cu(II) ions adsorbed onto Bt-Ch composites.
Note: Initial Pb and Cu concentrations 100 mg/L; pH = 4.5; adsorbent amount = 0.2 g; adsorption agitation time (at 230 rpm) = 10 minutes; desorbing agent = EDTA (0.01 mol/L); desorption agitation time (at 230 rpm) = 120 minutes. Each bar represents mean ± standard deviation of three (3) different samples (n = 3).

CONCLUSION

The simultaneous batch adsorption of Pb(II) and Cu(II) ions onto Bt-Ch composites from binary solutions were investigated. The adsorption equilibrium data correlated well with single-component Langmuir and Freundlich models. Also, the same equilibrium adsorption data fitted well with multi-component non-modified Langmuir, modified Langmuir and extended Freundlich model equations. The maximum adsorption capacities, Q_{max} (mg/g) of both Pb (II) and Cu (II) ions estimated for Bt-Ch composites were compared. The Q_{max} values obtained for Pb(II) ions were about 60% higher compared to values obtained for Cu(II) ions. Overall, the Bt-Ch composites exhibited good potential for re-use after five cycles of regeneration, thus, indicating their potential as cost-effective adsorbents for simultaneous removal of Pb (II) and Cu (II) ions from wastewater. Future studies could explore the column adsorption for simultaneous removal of these metal ions from binary solutions using the same adsorbent.

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REFERENCES

[1] W.S Wan-Ngah, S. Fatinathan (2009), Adsorption characterization of Pb(II) and Cu(II) ions onto chitosan-tripolyphosphate beads: Kinetic, equilibrium and thermodynamic studies. J Environ Manage, 91, 658–969.

[2] W. Liu, B. Ma, F. Li, Y. Fu, J. Tai, Y. Zhou, L. Lei (2016), Reduction of lead dioxide with oxalic acid to prepare lead oxide as the positive electrode material for lead acid batteries. RSC Adv, 6, 108513.

[3] J. Nonkumwong, S. Ananta, L. Srisombat (2016), Effective removal of lead(II) from wastewater by amine-functionalized magnesium ferrite nanoparticles. RSC Adv, 6, 47382.

[4] M.M Hassan, A.A Nuhu, M.S Sallau, H.M Majiya, A.K Mohammed (2015), Zamfara lead poisoning saga: Comparison of lead contamination level of water samples and lead poisoning in Bagega Artisanal gold mining district, Nigeria. J Chem Pharm Res, 7, 7–12.

[5] M.S Sallau, M.H Majiya, A.A Nuhu (2014), Mercury, Cadmium and Nickel Contamination Levels in Water Samples of Bagega Artisanal Gold Mining Communities: The Environmental Health Importance. Res. J. Pharm. Biol. Chem. Sci, 5, 531–536.

[6] A.A Nuhu, M.S Sallau, M.H Majiya (2014), Heavy Metal Pollution: The Environmental Impact of Artisanal Gold Mining on Bagega Village of Zamfara State, Nigeria. Res. J. Pharm. Biol. Chem. Sci., 5, 306–313.

[7] W. Meng-Wai, K. Chi-Chuan, B.D Rogel, M. Lourdes, P. Dalida (2010), Adsorption of copper (II) and lead (II) ions from aqueous solution on chitosan-coated sand. Carbohydr Polym, 80, 891–899.

[8] H. Majiya (2022), Remediation of Heavy Metals from Water using Modified Clay-Chitosan Composites. PhD Thesis, Sheffield Hallam University, United Kingdom.

[9] W.S Wan-Ngah, S. Fatinathan (2009), Adsorption characterization of Pb(II) and Cu(II) ions onto chitosan-tripolyphosphate beads: Kinetic, equilibrium and thermodynamic studies. J Environ Manage, 91, 658–969.

[10] H. Majiya, F. Clegg, C. Sammon (2023), Bentonite-Chitosan composites or beads for lead (Pb) adsorption: Design , preparation, and characterisation. Appl Clay Sci, 246, 107180.

[11] C. Hu, P. Zhu, M. Cai, H. Hu, Q. Fu (2017), Comparative adsorption of Pb(II), Cu(II) and Cd(II) on chitosan saturated montmorillonite: Kinetic, thermodynamic and equilibrium studies. Appl Clay Sci, 143, 320–326.

[12] R. El-Kaim-Billah, M.A Islam, M.K.Nazal, L. Bahsis, A. Soufiane, Y. Abdellaoui, A. Mounia (2024), A novel glutaraldehyde cross-linked chitosan@acid-activated bentonite composite for effective Pb (II) and Cr

ISSN 0795 - 22066

(VI) adsorption: Experimental and theoretical studies. Sep Purif Technol 334, 126094.

[13] J.D Cuppett, S.E Duncan, A.M Dietrich (2006), Evaluation of copper speciation and water quality factors that affect aqueous copper tasting response. Chem Senses. 31, 689–697.

[14] H. Majiya, F. Clegg, C. Sammon (2024), A chemometric approach using I-optimal design for optimising Pb(II) removal using bentonite-chitosan composites and beads. J Environ Manage., 370, 122557.

[15] M. Vakili, S. Deng, G. Cagnetta, W. Wang, P. Meng, D. Liu, G. Yu (2019), Regeneration of chitosan-based adsorbents used in heavy metal adsorption: A review. Sep Purif Technol., 224, 373–387.

[16] K.G Akpomie, F.A Dawodu, K.O Adebowale (2015), Mechanism on the sorption of heavy metals from binary-solution by a low-cost montmorillonite and its desorption potential. Alexandria Eng. J., 54, 757–67.

[17] E. Worch (2012), Adsorption Technology in Water Treatment: Fundamentals, Processes, and Modeling. 01062 Dresden Germany: De Gruyter, Inc.

[18] K. Y Foo, B.H Hameed (2010), Insights into the modeling of adsorption isotherm systems. Chem. Eng. J., 156, 2–10.

[19] V.C Srivastava, I.D Mall, I.M Mishra (2006), Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash. Chem. Eng. J., 117, 79–91.

[20] V.C Srivastava, I.D Mall, I.M Mishra (2009), Competitive adsorption of cadmium(II) and nickel(II) metal ions from aqueous solution onto rice husk ash. Chem. Eng. and Proc: Proc. Inten., 48, 370–379.

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