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Adsorption of Copper Ions from Aqueous Systems Using Moss Peat: Reaction Kinetics and Adsorption Isotherm

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Abstract: The removal of copper ions from aqueous systems using moss peat was investigated. Kinetic experiments were conducted at a constant temperature, pH, and initial copper concentration. The data obtained from the kinetic experiments were analysed and fitted well using the pseudo-second-order model. The data of the isotherm experiment were modelled and fitted well with the Langmuir models. This finding suggests that copper ions are chemically adsorbed on the moss peat and assume monolayer adsorption. The optimum pH for copper ion adsorption by moss peat was investigated over a range of (2-4.5), and it was found that the maximum adsorption capacity of moss peat was achieved at pH 4.5. The results of this study suggest the potential use of moss peat as an effective material for the adsorption of copper ions from aqueous solutions under a range of environmental conditions.

Keywords: Cu(II), Moss peat, Reaction kinetic, Adsorption isotherm

Introduction

Copper is a strategic element that is widely used in industries like metallurgy, fungicides, mining, electroplating, and petroleum refining (Demirbas et al., 2009; Trakal et al., 2014). However, improper disposal of industrial effluents has led to the release of copper ions, Cu^{2+}, into aquatic systems, causing toxic effects (Hossain et al., 2012b). Moreover, acute exposure to Cu^{2+} can result in several physiological issues in humans, including mental illness, schizophrenia, cardiovascular disease, Alzheimer's disease, and diseases of aging (Brewer, 2007; Faller, 2009; Hureau & Faller, 2009).

The remediation of contaminated water resources has recently attracted much interest due to the limited water resources and high water demand. There are various techniques for removing heavy metals from aqueous systems, such as cementation, reverse osmosis, electrochemical methods, and membrane filtration (Al-Saydeh et al., 2017). However, these techniques have drawbacks related to high operating costs, high energy consumption, or long duration (Gautam et al., 2014). Among these techniques, adsorption has received the most attention because of its simplicity, high removal efficiency, and cost-effective process (Davarnejad & Panahi, 2016).

The adsorption of heavy metals has been studied using a variety of adsorbents. However, carbon-rich adsorbents have shown several benefits due to their simplicity of use, availability, and environmentally friendly materials (Hossain et al., 2012a; Khatoon & Rai, 2016). Numerous studies have been carried out on the adsorption of metal ions from aqueous solutions using organic-rich adsorbents, such as banana peels, humic acid, grass, and sawdust (Rafatullah et al., 2009; Hossain et al., 2012a; Aldmour, 2018; Aldmour et al., 2019). It has been found that the adsorption capacities of these adsorbents vary significantly depending on their source. Therefore, further investigation of other adsorbents is required to assess their ability to adsorb Cu^{2+} under different conditions.

Materials and Method

Moss Peat

The Moss peat used in this study was collected from Kekkilä Professional (Kekkilä Professional, Finland), which produces moss peat for horticulture use. Air-dried and sieved moss peat (p.z 600-850 µm) was prepared and used for characterization tests. For the batch experiments, moss peat was oven-dried to a constant mass at 105 °C.

Characterization of Moss Peat

Moss peat was characterized by moisture, ash, and volatile matter contents. The moisture content of the moss peat samples was estimated as a percentage of the air-dried samples based on ASTM standard D2974-87, method A (ASTM, 1999). The ash content of moisture-free moss peat samples was determined according to ASTM standard D1102-84 (ASTM, 2001). After ignition at 600 °C, the ash content was calculated for moss peat as a percentage of the residue relative to the initial mass of moss peat. The volatile matter content was determined according to the ASTM standard E872-82 (ASTM, 2013). Moisture-free samples were heated at 950±20 °C for 7 min, and volatile matter was calculated as a percentage of mass loss relative to the moisture-free sample. All tests in this study were performed in triplicates.

Preparation of Copper Solution

A stock solution (400 mM) of Cu^{2+} was prepared by dissolving copper sulfate pentahydrate (CuSO4.5H2O; Sigma Aldrich) in deionized water. Copper-moss peat suspensions were prepared by diluting the stock solution with deionized water to obtain the target concentrations of Cu^{2+}. All chemicals used in this study were of analytical grade.

Batch Experiments

Effect of Contact Time

To prepare copper-moss peat suspensions, moss peat (2.5 g) was mixed with 237.5 ml of deionized water. The pH of the suspensions was adjusted to ~ 4.0, using 1 M HCl or 1 M NaOH, and periodically shaken until the pH of the suspensions remained stable for at least a day. Then, the copper solution (400 mM) was adjusted to pH 4, and 12.5 ml of this solution was added to each suspension to obtain a final volume of 250 ml, and the concentration of Cu^{2+} in the final suspensions was 20 mM (1270.9 mg/l)). The samples were then maintained at 20 ±1 °C with agitation at 150 rpm for 7 hr. Throughout the experiment, samples were periodically taken from the suspensions after 0.25, 0.5, 1.5, 2, 3, 4, 5, and 7 h and then filtered using a 0.45 µM PTFE syringe filter for Cu^{2+} analysis. The data obtained from this experiment were used to identify the optimum contact time for the adsorption of Cu^{2+} and were fitted to the sorption kinetic models.

Effect of Initial Concentration of Copper

The effect of the initial Cu^{2+} concentration on the adsorption process was determined over a range of 50–300 mg/l. The pH of the suspensions was adjusted to 4, and the adsorbent dosage was 4 g/l. The remaining experimental conditions were maintained as described in Section 2.4.1, and the experiment was conducted for a period equal to the optimum contact time determined in the contact time experiment (Section 2.4.1). At the end of the experiment, the samples were collected, filtered, and analyzed for the Cu^{2+} concentration in the solution. The data obtained from this experiment were fitted to sorption isotherm models.

Effect of Initial pH

The effect of pH on the removal of Cu^{2+} from aqueous systems was studied over a pH range of 2.0 to 4.5. To adjust the initial pH of the suspensions, 1 M HCl or 1 M NaOH was used. The other experimental conditions were maintained as described in Section 2.4.1. At the end of the experiment, the samples were withdrawn, filtered, and analyzed for Cu^{2+} concentration in the solution. All batch experiments were performed in triplicates.

Copper Analyses

The residual Cu^{2+} in the aqueous solutions was measured using Atomic Absorption Spectrometry (AAS-7000 Shimadzu). A calibration curve for Cu^{2+} was constructed within the range of 0.1-2.0 mg/l using a copper standard solution obtained from Sigma-Aldrich.

Results and Discussion

Characterization of Moss Peat

The characterization of moss peat is summarized in Table 1. It was found that moss peat has a low ash content of 6.4%. In contrast, the volatile organic matter was very high. These results suggest that the large organic fraction in moss peat may play a significant role in metal adsorption. Previous studies pointed out that organic-rich materials like sewage sludge, mosses, and soil organic matter have a high content of functional groups and consequently have an abundance of binding sites for metal interaction (Won et al., 2013; González & Pokrovsky, 2014; Aldmour, 2018). Accordingly, moss peat may have a high adsorption capacity for Cu^{2+}.

Table 1 Characterization of moss peat

	Moss peat
Moisture content	54.3±0.87
Ash content (wt.% dry basis)	6.54±0.34
Volatile matter (wt.% dry basis)	92.40±0.12

Effect of Contact Time

The percentage of copper adsorbed by moss peat was calculated using the following equation:

$$\%Removal = \frac{C_o - C_e}{C_o} \times 100\% \ldots\ldots\ldots\ldots\ldots (1)$$

Where: C_o and C_e are the initial and equilibrium concentrations of metal ions in the solution (mg/l), respectively. Figure 1 illustrates the impact of contact time on the percentage of Cu^{2+} removal using moss peat. It was found that within the initial 30 minutes, a rapid rate of Cu^{2+} absorption was observed, followed by a relatively slow rate until reaching the equilibrium state at 240 min. The experiment revealed that 29.2% of Cu^{2+} was removed from the solution within 30 minutes, while only 4.3% was removed within 210 minutes. These results may be due to the abundance of active sites on the adsorbent surface during the initial stage of the reaction, while the decrease in reaction rate can be attributed to limited binding sites as the reaction progresses (Kowanga et al., 2016).

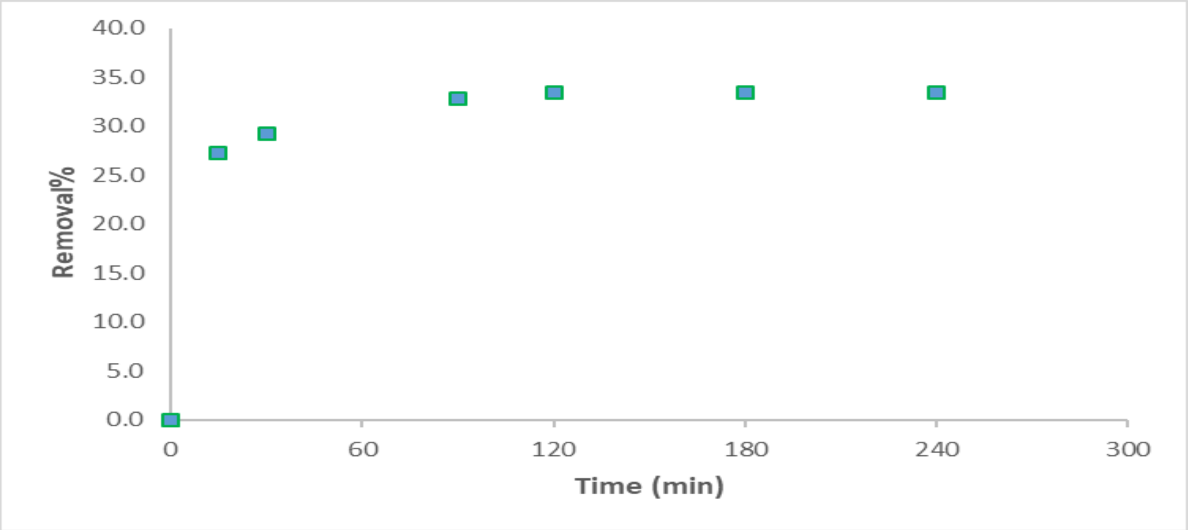

Figure 1. Percentage of Cu^{2+} removal from aqueous solution by moss peat versus time

Kinetics

The sorption mechanism and kinetic parameters were investigated using pseudo-first-order and pseudo-second-order models. The pseudo-first-order equation is expressed in its linearized form by the following equation:

$$log(q_e - q_t) = logq_e - \frac{k_1}{2.303}t \ldots\ldots\ldots\ldots\ldots (2)$$

Where: qe is the amount of metal ions adsorbed per unit mass of adsorbent at equilibrium (mg/g), q_t is the amount of metal ions adsorbed per unit mass of adsorbent at variable time (mg/g), k_1 is the rate constant of the pseudo-first-order kinetic model (min^{-1}), t is the time (min). A plot of $\log(q_e-q_t)$ versus t results in a straight line, and the values of a slope and intercept are used to determine the values of k_1 and q_e, respectively.
The linearized form of the pseudo-second-order kinetic equation is expressed by equation 3:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \ldots\ldots\ldots\ldots\ldots (3)$$

Where: k_2 is the rate constant of the pseudo-second-order model (g/mg.min). A plot of t/q_t versus t gives a straight line, and the values of q_e and k_2 are calculated from the slope and intercept, respectively. The kinetics parameters of the pseudo-first-order and the pseudo-second-order models for the adsorption of Cu^{2+} on moss peat were calculated using Figures 2 and 3 and presented in Table 2. The correlation coefficient for the pseudo-second-order model was significantly greater than that for the pseudo-first-order model. This finding suggests that the pseudo-second-order model can describe the adsorption of Cu^{2+} on moss peat.

Table 2. Kinetic parameters of pseudo-first-order and pseudo-second-order models

Sorbent	Pseudo-First Order Calculated q_e (mg/g)	K_1 (min^{-1})	R^2	Pseudo-Second Order Calculated q_e (mg/g)	K_2 (min^{-1})	R^2
Moss Peat	7.77	0.0039	0.7581	61.35	0.0028	0.9989

Figure 2. Pseudo-first order kinetic model for the adsorption of Cu^{2+} on moss peat

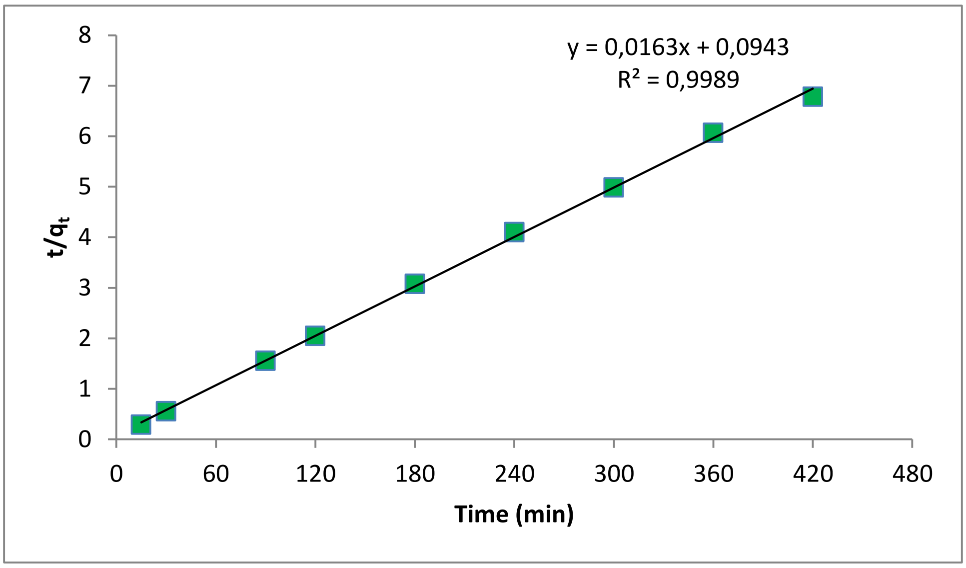

Figure 3. Pseudo-second order kinetic model for the adsorption of Cu^{2+} on moss peat

3.3 Adsorption Isotherms

Isotherm models were used to understand the adsorption mechanism of Cu^{2+} on moss peat and its maximum adsorption capacity. The two most common isotherm models, including Freundlich and Langmuir, were applied to fit the data. The Freundlich isotherm equation is expressed in its linearized form by the following equation (Wang & Guo, 2020):

$$log q_e = log K_F + \frac{1}{n} log C_e \dots\dots\dots\dots\dots (4)$$

Where: q_e (mg/g) is the amount of sorbate per unit mass of sorbent at equilibrium, C_e (mg/l) is the concentration of sorbate in the liquid phase at equilibrium, K_F ((mg/g)(L/mg)$^{1/n}$) is the Freundlich adsorption constant, and n (dimensionless) is an empirical parameter related to the adsorption intensity (Kılıc et al., 2013). A plot of log q_e versus log C_e gives a linear relationship, and the values of n and K_F were calculated from the slope and intercept, respectively. The linear form of the Langmuir isotherm equation is written as follows (Wang & Guo, 2020):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \dots\dots\dots\dots\dots (5)$$

Where: q_m (mg/g) is the maximum adsorption capacity of adsorbents calculated by Langmuir model, and K_L (L/mg) is the rate adsorption constant (adsorption rate to desorption rate ratio). The plot of C_e/q_e versus C_e yields a straight line, which is used to estimate q_m and K_L values from the slope and intercept, respectively. These parameters, q_m and K_L, are then used to estimate the separation factor, R_L (dimensionless), which predicts the affinity between the metal ion and the adsorbents. R_L is calculated using the following equation (Weber & Chakravorti, 1974; Kowanga et al., 2016):

$$R_l = \frac{1}{1 + K_L C_o} \dots\dots\dots\dots\dots (6)$$

Where: C_o (mg/l) represents the highest initial concentration of the adsorbate in the solution. Based on the value of R_L (R_L>1, R_L=1, 1>R_L>0, R_L=0), the adsorption process can be categorized as unfavorable, linear, favorable, and irreversible, respectively. The parameters obtained from the Langmuir and Freundlich models are presented in Table 3. The correlation coefficients (R^2) of the Freundlich and Langmuir models were determined to be 0.863 and 0.992, respectively. The findings of this study indicate that the equilibrium adsorption data is fitted well in the Langmuir isotherm model. This finding demonstrates that Cu^{2+} undergoes chemical adsorption on the adsorption sites of moss peat, suggesting homogeneous monolayer adsorption. Also, it was found that moss peat has a high adsorption capacity of 23.42 mg/g, which might be attributed to its high organic content. It must be pointed out that organic-rich materials with low ash content showed a high adsorption capacity for adsorbates, while those with a high ash content exhibited a low adsorption potential for adsorbates due to the covering of organic moieties by ash (Zhang et al., 2013; Inyang & Dickenson, 2015).

Table 3. Langmuir and Freundlich isotherm parameters

Adsorbent	Langmuir isotherm				Freundlich isotherm		
	q_m	K_L	R_L	R^2	N	K_F	R^2
Moss peat	23.42	0.0726	0.044	0.992	3.632	5.574	0.863

Table 4. Maximum Cu^{2+} adsorption capacity using biomass adsorbent

Adsorbent	pH	Temperature (ºC)	Dosage of adsorbent (g/l)	Maximum Adsorption capacity (mg/g)	Reference
Cellulose pulp waste	<6	22	20	4.98	(Ulmanu et al., 2003)
Active carbon	<6	22	20	6.61	(Ulmanu et al., 2003)
Compost	7.3	22	20	12.77	(Ulmanu et al., 2003)
Corn straw- biochar	5	20 ± 2	5	12.52	(Chen et al., 2011)
Hard wood-biochar	5	20 ± 2	5	6.79	(Chen et al., 2011)
Tree fern	NA*	20	5	10.6	(Ho et al., 2002)
Hazel nut husk-activated carbon	5.7	18	(2-20)	6.65	(Imamoglu & Tekir, 2008)
Moss peat	4	20 ± 1	4	23.42	This study

*NA: Not available

When comparing the maximum adsorption capacity of Cu^{2+} on moss peat to those of previous studies (see Table 4), it is noted that the adsorption capacity of moss peat is significantly higher than that of many organic-rich adsorbents. As a result, this study suggests that moss peat may have an important implication as an adsorbent for the remediation of Cu^{2+} contaminated water. The value of R_L was determined, and it was less than 1. This result indicates that the adsorption of Cu^{2+} on moss peat is a favorable process.

Effect of pH on Copper Adsorption

pH is an important factor that influences the adsorption of metals onto sorbent surfaces. The pH has been found to have an impact on the speciation of metals in aqueous solutions, the ionic state of functional groups, the surface charge, and the characteristics of the sorbent (Hossain et al., 2012a; Yu et al., 2013). The impact of the initial pH of the suspension on the adsorption of Cu^{2+} by moss peat was examined within the pH range of 2–4.5. Within this range, copper predominantly exists in the form of Cu^{2+}, and the hydrolysis and precipitation of copper ions are not observed (Kołodyńska et al., 2012). Figure 6 shows an increase in the adsorption of Cu^{2+} by moss peat as the pH increased from 2.0 to 4.5. The maximum adsorption capacity of moss peat was observed at pH 4.5, with a value of 60.0 mg/g. The limited adsorption of Cu^{2+} at low pH can be attributed to the high concentration of hydrogen ions, which compete with Cu^{2+} for the available active sites. As the pH increases, there is a corresponding decrease in the amount of hydrogen ions, resulting in an increased availability of binding sites for Cu^{2+}.

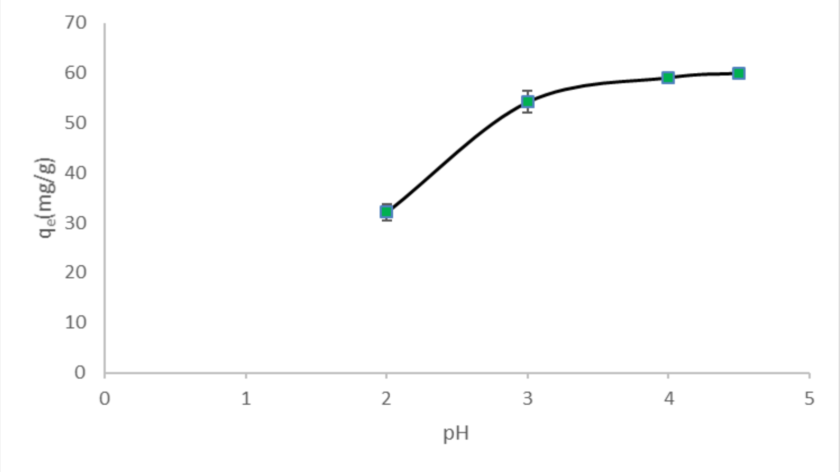

Figure 6. Effect of pH on the adsorption of Cu(II) by moss peat

Conclusion

In this research study, moss peat, the fibrous product of the anaerobic decomposition of sphagnum moss, effectively removed Cu^{2+} from aqueous solutions. A pseudo-second-order could fit the kinetic experimental data. Moreover, the Langmuir model fitted the adsorption isotherm data well, suggesting that Cu^{2+} was adsorbed chemically for the binding sites at moss peat. By comparing the adsorption capacity of moss peat for the adsorption of Cu^{2+} with other organic-rich adsorbents, moss peat can be used as an effective adsorbent under the studied environmental conditions.

Scientific Ethics Declaration

The author declares that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the author.

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