Adsorption Behavior of Cu(II) Ions on Thermally-Treated Peat of Muthurajawela, Sri Lanka

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Abstract

Muthurajawela peat (MP), being organic in nature, undergoes many physical and chemical transformations when subjected to heat treatment, as evident by Fourier transform infrared spectroscopic and thermogravimetric measurements. Thus, treatment temperature of peat is a crucial parameter to be optimized for metal sorption studies, which is determined to be 200 °C for Cu(II) removal. At lower temperatures, pores are not sufficiently exposed, while higher temperatures lead to the combustion of organic matter restricting complexation with Cu(II) ions. Investigation of the effect of shaking time and settling time on the extent of Cu(II) removal by MP treated at 200 °C leads to optimum values of 2.5 h and 1.0 h, respectively. Adsorption equilibrium studies of Cu(II) solutions on MP at different solution temperatures verify the suitability of the Freundlich adsorption isotherm, while kinetics data lead to the validity of the pseudo second order model. Adsorption studies of Cu(II) on humic acid, extracted from MP (M-HA) and pre-fired at 200 °C, performed under ambient pH provide evidence that humic acid plays a major role in the Cu(II) removal process, and that the Freundlich isotherm is satisfied better than the Langmuir model. The positive standard enthalpy change (ΔH^0_{ads}) for adsorption of Cu(II) on both MP and M-HA suggests the endothermic nature of the removal process.

Keywords: *Peat; humic acid; copper; adsorption; thermodynamics; kinetics.*

1. Introduction

The composition of peat varies considerably depending on its age, nature of the vegetation, regional climate, pH of the surrounding water and degree of metamorphosis. Many parameters, such as decomposition rate, organic matter content, humic and fulvic acid contents, and surface features can be used to characterize peat [1-4]. Humic acid (HA) is a heterogeneous mixture of complex aromatic compounds. Spectroscopic methods have been used to identify the structural behavior and distribution of HA, extracted from various sources, such as peat, landfill leachates, salt marsh soil, sediments and fresh water [5-8]. Anodic stripping voltammetric studies have demonstrated bond formation between metal ions and humic substances, and the covalent character of the bond increases with increasing the softness of the metal ion [9]. Further, potentiometric titrations of humic acids have indicated that the carboxylic acid content is much higher than the phenolic content, and the ratio between these two types of acidic components depends on the nature of humic acid, which subsequently influences the proton binding affinity [10]. It has also been reported that the ionization of carboxylic and phenolic groups present in HA plays a major role in increasing its thermal stability [11].

Adsorption of Pb, Cd and Cu on Danish and Heilongjiang peat in China shows the validity of pseudo second order kinetics for adsorption in single and multi-ion systems [12]. Peat obtained from Ireland is found to remove Cu and Ni with adsorption capacities of 17.6 mg g⁻¹ and 14.5 mg

g^{-1}, respectively [13], while poorly humified Sphagnum and Carex peat have shown the removal of Cu and Zn with capacities of 18.1 mg g^{-1} and 12.7 mg g^{-1} [14]. On the other hand, Cr(VI) has been removed by commercially available *Sphagnum* peat in Romania and peat in Brazil under various conditions, such as contact time, solution pH and dosage of peat [3,14]. It has also been reported that HA is more efficient in the removal of Cr(VI) than unprocessed peat due to its greater humification [3]. The strong affinity of peat towards metal ions is attributed mainly to the presence of phenolic and carboxylic groups in compounds present in peat. It is also argued that, though peat is rich in organic matter, it can be considered as another type of soil, as it possesses properties similar to those of soil, such as trapping cationic species into cavities and interlayer spacing [4]. Owing to these properties, peat has a great potential to be used as an effective treatment agent for waste water contaminated with heavy metal ions.

Most of the studies reported on removal of heavy metal ions by peat have utilized its natural form as a cost-effective, naturally available adsorbent although some attempts have been taken to improve the usage of peat by employing its modified forms [12, 15, 16]. Different forms of processed peat, such as acid-treated, thermally-treated or washed, have been used in several studies in order to enhance its adsorption properties [13, 15].

Interaction of metal ions with different components of peat has been studied recently in an attempt to understand the mechanism of interaction. For instance, adsorption of Cd(II) on HA coated with TiO$_2$ has shown to satisfy the Freundlich adsorption isotherm [17]. Further, complexation of HA and Fe(III) is induced by charge compensation of HA colloids on metal loading, as confirmed by time dependent UV/Vis spectroscopic data and solution pH measurements [6]. Such studies can be extended for effective removal of metal ions from industrial effluents.

Among many industrially important metals, Cu(II) is abundant, and thus, it could be present at levels higher than the regulatory permissible value. Consequently, removal of Cu(II) from aqueous solution is a necessity. In this context, the objective of this study is to investigate the adsorption behavior of Cu(II) on Muthurajwela peat (MP), with possible extension toward large-scale applications of heavy metal removal by this naturally available substance. Further, detailed investigation of thermodynamics and kinetics of Cu(II) removal by thermally treated MP, and comparison of thermodynamics with humic acid extracted from MP (M-HA) are also reported.

2. Materials and Methods

2.1 Materials and Sample Preparation

Peat obtained from Muthurajawela was ground well, sieved to obtain particles of diameter (d) < 1 mm, and homogenized. Analytical grade CuSO$_4$ (BDH Chemicals) was used to prepare standard solutions in de-ionized water. A sample of commercial HA (Sigma-Aldrich) was donated from a national laboratory in Sri Lanka. It was used to compare spectral features with those of HA extracted from Muthurajawela peat (M-HA), which was used in Cu(II) removal experiments.

2.2 Instrumentation and Experimental Design

Fourier transform infrared (FTIR) spectra were recorded on Thermo Nicolet Model-Avater 320 FTIR spectrophotometer, while scanning electron microscopic (SEM) images were taken using Oxford Instruments – EVO LS 15 (Zeiss) instrument. The Carbolite CTF 12/100/900 furnace was used to treat MP and M-HA samples. Metal ion concentrations in the studies of optimization, thermodynamics and kinetics were determined using either Spectro-Electronic M Series atomic absorption spectrophotometer (AAS), or Shimadzu AA-6701F atomic absorption - flame emission spectrophotometer. X-ray fluorescence analysis (XRF) was performed with XRF PANanalytical

Axios instrument, while thermogravimetric analysis (TGA) was performed using Scinco STA N-650 at a heating rate of 10 °C min^{-1}. All optimization, equilibrium and kinetics experiments were performed in triplicate at the ambient solution temperature of 298 K (unless otherwise indicated), and the average values were used in the interpretation.

2.3 Optimization of Parameters

Temperature of treatment, shaking time and settling time of the Cu(II) – MP system were optimized in order to study the removal efficiency of Cu(II). Effect of pH of solutions on the extent of removal was studied within the pH range of 2.0-8.0 under the optimized conditions. Removal efficiency for each experiment was calculated using Equation (1).

$$\text{Removal percentage} = \frac{(C_0 - C_f)}{C_0} \times 100 \tag{1}$$

where C_0 (mg L^{-1}) and C_f (mg L^{-1}) are the concentrations of Cu(II) in solution initially and after adsorption, respectively.

2.4 Extraction of M-HA, Its Characterization and Removal of Cu(II)

M-HA was extracted from MP with 0.50 M NaOH using the procedure described elsewhere [18] except that the speed of centrifugation used was 4500 rpm.

FTIR and UV/Vis spectroscopic techniques were used to characterize M-HA extracted. Characterization of M-HA by FTIR was carried out against commercial HA. Studies of Cu(II) – M-HA interaction at ambient pH and temperature were performed at 150 rpm with the help of an orbital shaker for a period of 3.0 h followed by 0.5 h settling time [18].

2.5 Investigation of Kinetics

For kinetics studies, 600 mL aliquots of Cu(II) solutions of 10.0 mg L^{-1} concentration were treated with 60.0 g of peat fired at 200 °C. While the solution was being stirred, 10.00 mL aliquots were withdrawn at every one minute interval up to 20 min, followed by withdrawals at 10 min time intervals until equilibrium was reached at 1.0 h.

2.6 Investigation of Thermodynamics and Adsorption Isotherms

Isotherm studies were carried out for Cu(II) solutions of concentrations varying from 10.0 mg L^{-1} to 1000 mg L^{-1}. The extent of sorption of Cu(II) for each initial concentration was determined by analyzing the supernatant solution for remaining Cu(II) after the adsorption equilibrium was established at ambient temperature under the optimized conditions. Sorption experiments using selected concentrations of Cu(II) were repeated under optimized conditions at different solution temperatures in order to study thermodynamics parameters.

3. Results and Discussion

3.1 Characterization of MP and M-HA

FTIR spectra obtained for MP samples fired at different temperatures are shown in Figure 1 as the extent of absorption vs. wave number. Similar spectral features have been reported for peat available in different countries although not much attention has been paid on fired peat [2,19]. Decrease in intensity or disappearance of peaks attributed to organic functional groups is clearly evident when the firing temperature is increased. This is due to combustion of organic compounds present in MP upon firing.
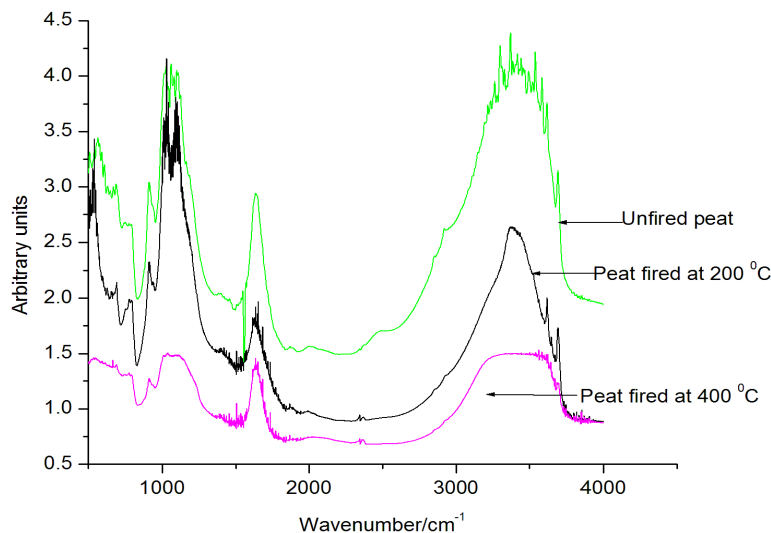
Figure 1. FTIR spectra of unfired peat, peat fired at 200 °C and peat fired at 400 °C.

Table 1 lists specific organic compounds/functionalities that could be present in MP, based on spectral evidence. Further, both MP and M-HA lost 65-70% of their mass upon heat treatment up to 500 °C according to mass differences obtained from TGA results, indicating their highly organic nature. This is further supported by the fact that exothermic reactions occur between the firing temperatures of 100 – 500 ºC according to TGA results. However, owing to the presence of large organic molecules which are not decomposed up to 500 ºC, complete mass loss cannot be excepted unless higher temperatures are employed [20]. Together with the loss of organic matter upon firing, adsorption pores and sites in MP increase and expand, improving adsorption characteristics, as evidenced by SEM images of MP fired at different temperatures (Figure 2).

Table 1. Functional groups present in peat.

Peak/cm^{-1}	Possible functional groups
3100-3600 (broad)	Monomeric alcohol, phenol, H-bonded alcohol, carboxylic acid
1095	Alcohol, ether, carboxylic acid, ester
1041	C-H
916	$RCH=CH_2$
789	Mono-substituted aromatic compounds

Comparison of spectral characteristics of M-HA and commercially available HA indicates the reasonable purity of the extracted substance (Figure 3). The broad peak in the range of 3100 cm^{-1} and 3500 cm^{-1} indicates the presence of –OH and –COOH groups, while that of 1500 to 2000 cm^{-1} indicates the presence of aromatic C-C bonds.

3.2 Optimization of Experimental Conditions

The extent of removal of Cu(II) from solution at ambient temperature by MP fired at different temperatures ranging from 100 – 900 °C indicates that the highest removal of Cu(II) is obtained with MP fired at 200 °C. Sorption experiments conducted with MP fired at 200 °C, the optimum firing temperature, by varying the shaking time and the settling time separately within a broad range of each parameter indicate that a shaking time period of 2.5 h and a settling time period of 1.0 h provide the highest removal. Therefore, subsequent adsorption equilibrium studies were

conducted with MP using these optimum conditions. The pH of the medium was maintained at the ambient values of 3.5 - 4.0 for MP and 4.0 – 5.0 for M-HA in sorption experiments. The medium pH would significantly change the uptake of Cu(II) by the adsorbent, M-HA or MP [13,15,21]. Nevertheless, there was no significant increase in the extent of Cu(II) uptake beyond this pH, although it was decreased at lower pH values due to the competition of H_3O^+ ions. It has already been reported that the favorable pH range for interaction of Cu(II) with Irish peat is 4.0 – 4.5, supporting the pH maintained during this study [13].
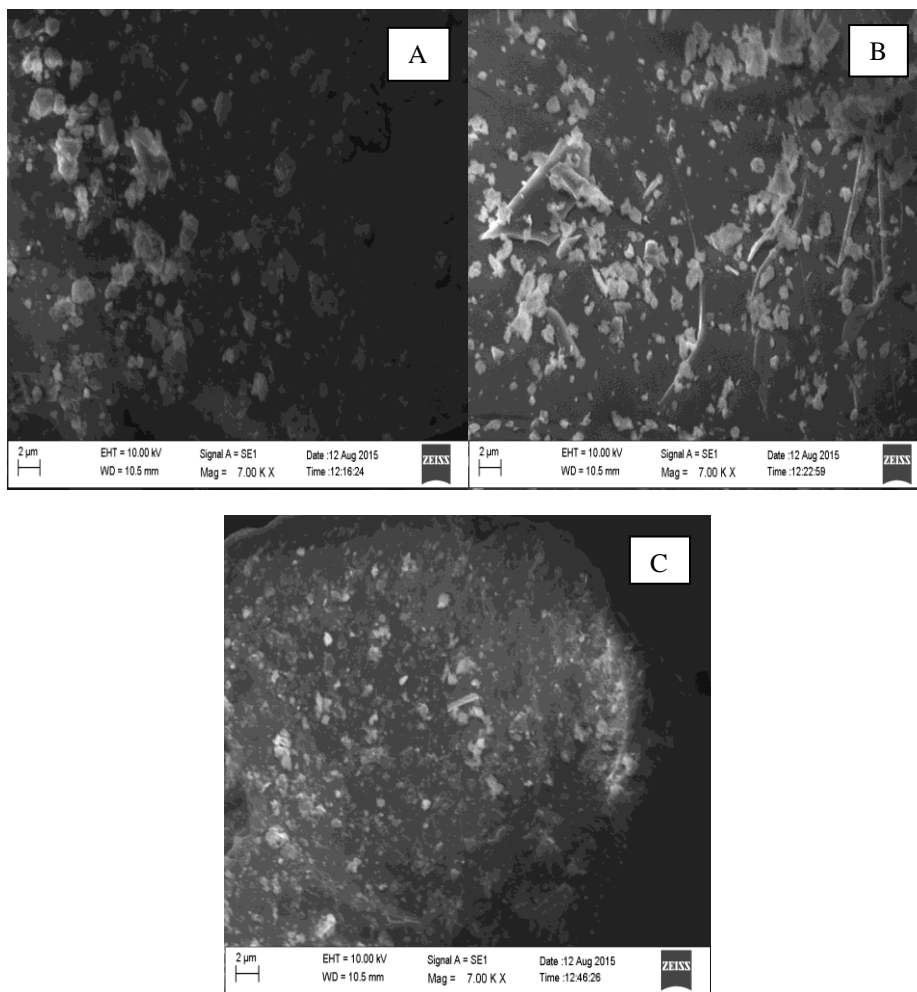

Figure 2. SEM images of MP (A), MP fired at 200 °C (B), followed by treatment with Cu(II) (C) (5.00 g peat, 50.0 mL of 1000 mg L^{-1} Cu(II) solution, optimized shaking and settling time).

3.3 XRF Spectroscopic Investigation of Interaction of Cu(II) with MP and M-HA

XRF spectroscopy is a non-destructive method which is able to determine metallic constitutents present in a sample. MP fired at 200°C without any treatment with Cu(II) does not contain any Cu according to XRF spectroscopic results, while MP after treatment with 1000 mg L^{-1} Cu(II) shows the presence of Cu in the XRF spectrum together with decrease in line intensity of Na, Mg and Ca. This observation suggests that Cu(II) from solution is sorbed on MP, probably replacing Na, Mg and Ca. Similar observations of ion exchange reactions of peat have been reported for several metal ions supporting the above findings [15,22]. In addition to ion-exchange, complexation of Cu(II) with –OH and –COOH moieties in M-HA/MP would also provide another mode of mass

transfer. This is supported by previous reports on complexation of Cu(II) with peat and humic acid [15,23].
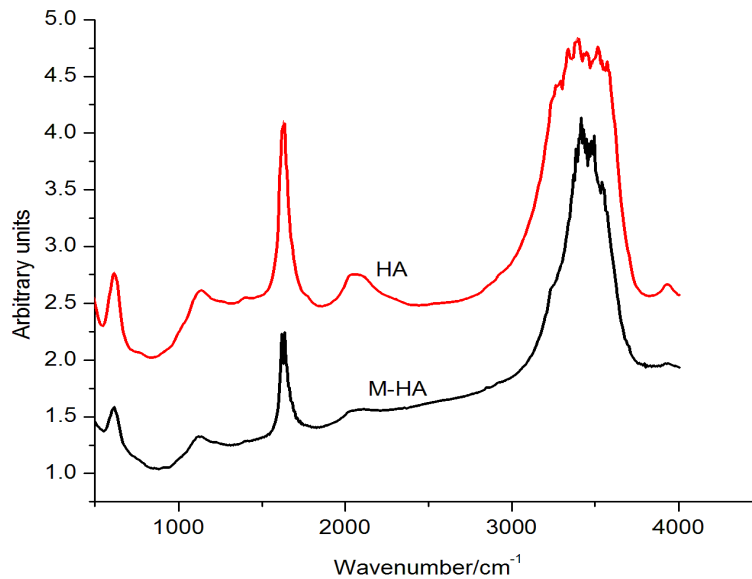

Figure 3. FTIR spectra of M-HA and commercial HA.

3.4 Investigation of Adsorption Isotherms

The amount of Cu(II) adsorbed on fired MP from aqueous solution continuously increases with the initial concentration at different solution temperatures indicating the strong affinity of MP towards Cu(II) (Figure 4). In order to assess the mode of adsorption and the adsorption capacity of MP, the Langmuir and Freundlich adsorption isotherms can be used [24]. The linear forms of these isotherms are

$$\frac{1}{q_e} = \frac{1}{bq_{max}}\left(\frac{1}{C_e}\right) + \frac{1}{q_{max}} \qquad (2)$$

and

$$\ln(q_e) = n\ln(C_e) + \ln K_f \qquad (3)$$

where C_e is the concentration of metal ion in solution phase at equilibrium, q_e is the amount of Cu(II) transferred from solution to adsorbent phase (mg kg^{-1}) at equilibrium, b is the isotherm constant and q_{max} is the adsorption capacity (mg kg^{-1}) which is a measure of the extent of adsorption on an adsorbent. In the above models, b is the isotherm constant of the Langmuir model which is equivalent to the equilibrium constant of adsorption, while n and K_f are Freundlich isotherm constants.

Langmuir and Freundlich isotherm models are applied to adsorption systems in order to get an insight of the adsorption mechanism and to identify whether adsorption would result in monolayer or multilayer coverage [24]. Experimental data obtained for Cu(II) adsorption within a wide concentration range when plotted according to the linearized forms of the Langmuir and Freundlich isotherms are shown in Figure 5 at a solution temperature of 298 K. Adsorption isotherms constructed at other solution temperatures produce similar results, and hence only isotherm constants and regression coefficients evaluated are given in Table 2. The n values being between 0 and 1 are indicative of favorable adsorption of Cu(II) on MP within solution temperatures of 298 – 323 K, while high K_f values further support the availability a large number of active sites for sorption of Cu(II) [25].
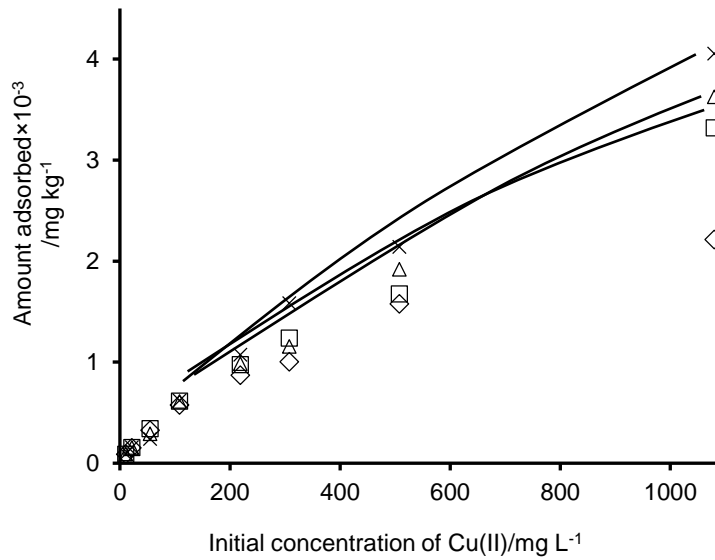
Figure 4. Amount of Cu(II) sorbed on MP fired at 200 °C at different solution temperatures of 293 K (--◇---), 303 K (□--□--), 313 K (--Δ--) and 323 K (--×--) [5.00 g peat, 50.0 mL Cu(II) solution, 2.5 h shaking, 1.0 h settling].

Table 2. Isotherms parameters for removal of Cu(II) by MP fired at 200 °C at different solution temperatures.

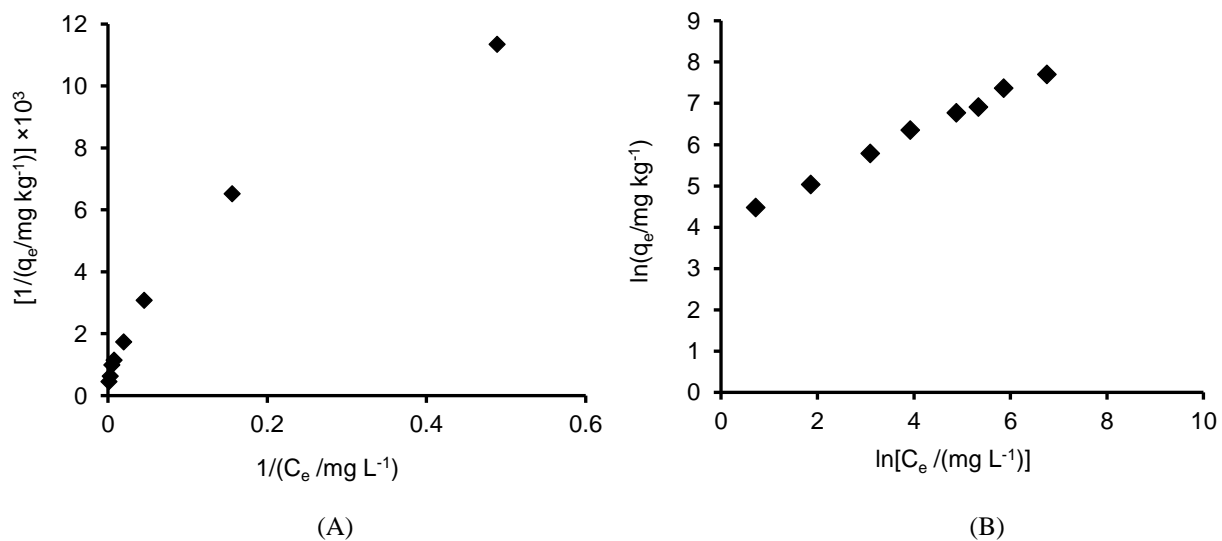| Temperature/K	Langmuir isotherm			Freundlich isotherm		
	$b/$ $L\ mg^{-1}$	q_{max} $/mg\ kg^{-1}$	R^2	n	K_f $/mg\ kg^{-1}$	R^2
293	0.05	833	0.943	0.545	60	0.995
303	0.06	833	0.932	0.594	58	0.995
313	0.09	714	0.883	0.600	57	0.979
323	0.12	666	0.841	0.641	53	0.949

(A)

(B)

Figure 5. Langmuir (A) and Freundlich (B) isotherm models for adsorption of Cu(II) on MP fired at 200 °C at a solution temperature of 298 K [5.00 g peat, 50.0 mL Cu(II) solution, 2.5 h shaking, 1.0 h settling].

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High regression constants associated with the Freundlich isotherm reveal that the amount of Cu(II) removed from the solution phase is more than what is required for monolayer coverage, indicating that excess Cu(II) after completion of the monolayer would transfer to the bulk MP matrix owing to the clay properties of peat [26]. Further, increase in isotherm constants of the Freundlich model with increase in solution temperature suggests the endothermic nature of the process. Similar observations have been reported for adsorption of Cu(II) on peat of Brunei Darussalam [27].

3.5 Investigation the Removal Ability of Cu(II) by M-HA

The average amount of humic acid extracted from MP is approximately 16% (W/W), indicating that the mass ratio of M-HA to MP that should be used for comparative adsorption studies is 1:6. It is clear from Figure 6 that M-HA shows a stronger affinity for Cu(II) as compared to MP. As shown in the figure, the extent of removal of Cu(II) by M-HA, and MP fired at 200 °C is determined at the ambient pH of 4.0-5.0 within the initial Cu(II) concentration range from 2.0 mg L^{-1} to 120.0 mg L^{-1} increases with the initial concentration of Cu(II). Further, it is observed that the extent of removal of Cu(II) with respect to M-HA is leveled off at an initial concentration of about 20 mg L^{-1} indicating the completion of the formation of the monolayer, followed by an increase in the extent of adsorption beyond 60 mg L^{-1} supporting the validity of the Freundlich isotherm. Although linearized Langmuir isotherm and the Freundlich isotherm do not fully obey ($R^2 = 0.853$ and 0.792 for the two isotherms, respectively), adsorption capacity of M-HA toward Cu(II) is determined to be 6000 mg kg^{-1} as compared to 833 mg kg^{-1} for MP. The much higher value of M-HA could be attributed to combination of many chemical or physical processes, including ion exchange, adsorption and complexation. It can therefore be stated that the composition of peat with regard to humic acid, which varies depending on geographic and climatic conditions, has a strong influence on Cu(II) sorption leading to different values.

3.6 Kinetics studies

Adsorption systems involving natural adsorbents are usually characterized by pseudo first order, second order and pseudo second order kinetics models. Kinetic models are important in predicting the mechanism, including the rate controlling step. The linearized forms of the above models are given by

$$\log(q_e - q_t) = -\frac{k\prime}{2.303}t + \log(q_e) \tag{4}$$

$$\frac{1}{q_e - q_t} = k't + \frac{1}{q_e} \tag{5}$$

and

$$\frac{t}{q_t} = \frac{1}{q_e}t + \frac{1}{k\prime q_e^2} \tag{6}$$

respectively, where $k\prime$ is apparent rate constant, t is contact time, and q_e and q_t are the mass of Cu(II) sorbed by unit mass of sorbent at equilibrium and at time t, respectively. As q_t is more conveniently expressed in mg of Cu(II) sorbed by 1.0 kg of peat fired at 200 °C, the apparent rate constant $k\prime$ is estimated in kg mg^{-1}min^{-1} for pseudo second order reactions. Graphical representations of kinetics models, constructed for the interaction of Cu(II) with peat fired at 200 °C are shown in Figure 7. Large solution volumes, maintaining the 1:10 ratio between the adsorbent dosage and solution volume, were used in kinetics experiments to assure that the volume change is not significant after the withdrawal of samples for analysis at different time periods.
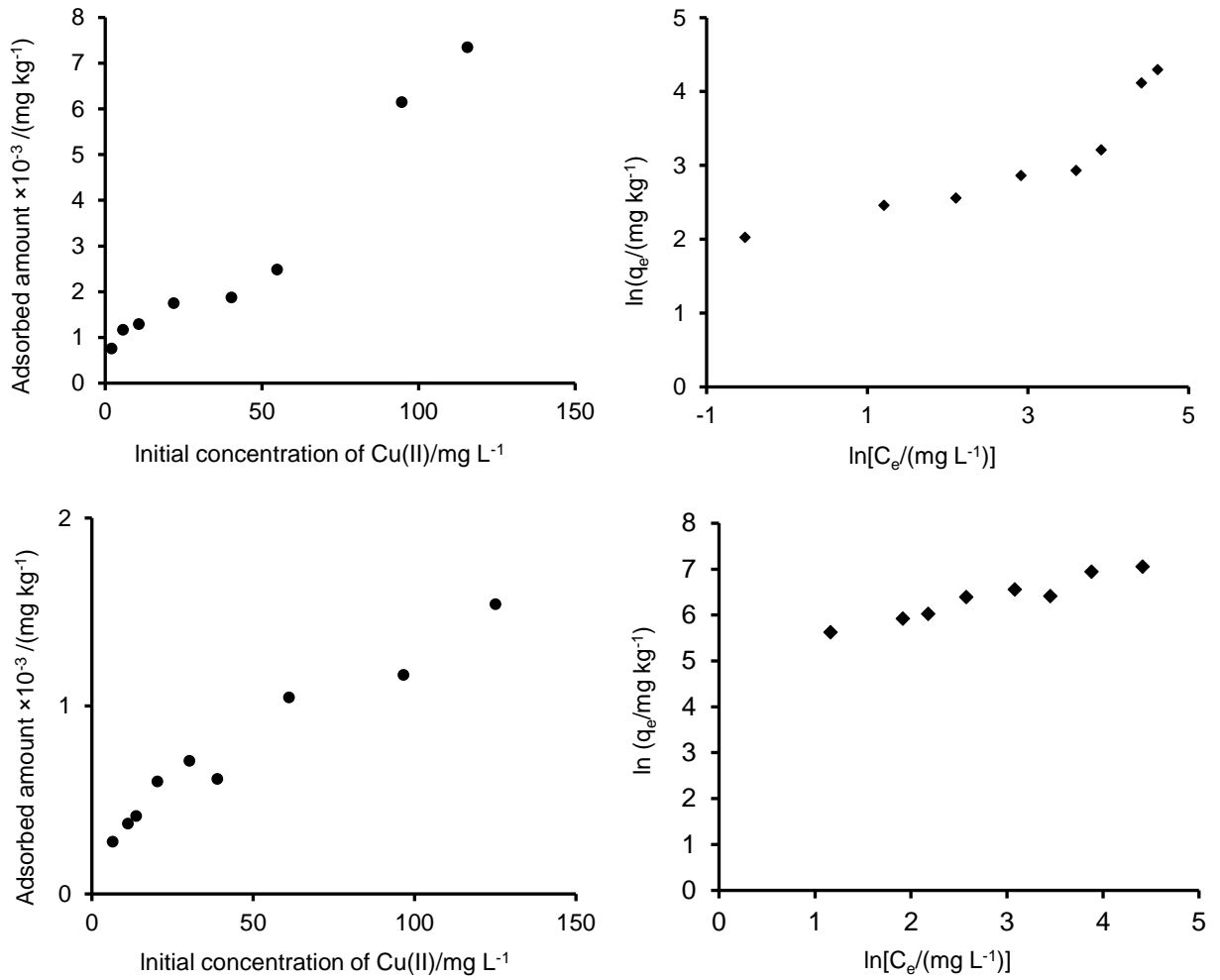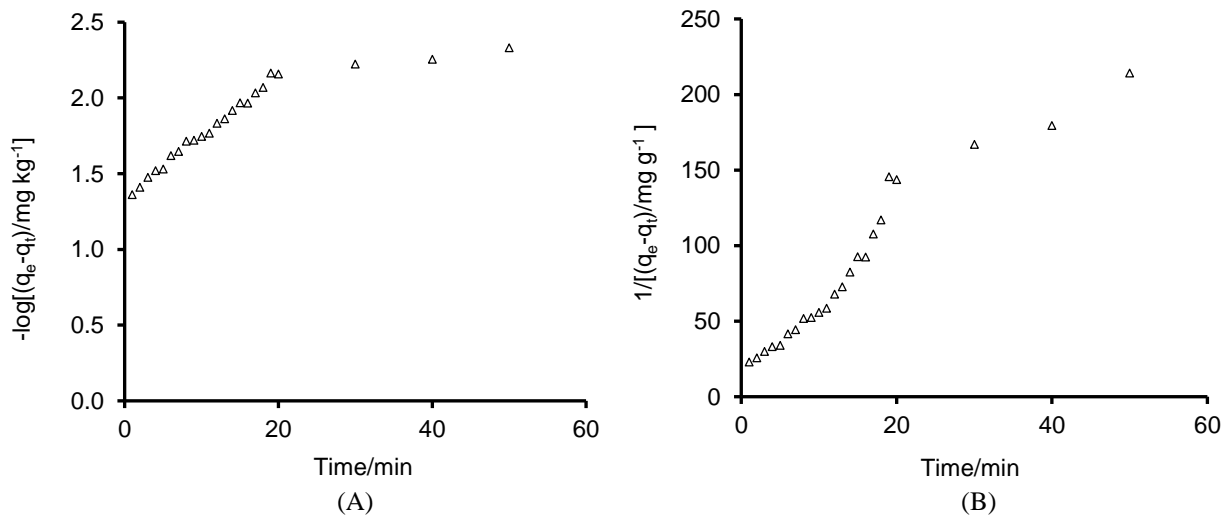
Figure 6. Adsorption patterns of Cu(II) on M-HA (top) and MP (bottom). Variation of the extent of adsorption with initial concentration of Cu(II) (left) and Freundlich isotherm model (right) [0.10 g M-HA or 0.60 g MP, 50.0 mL Cu(II) solution, 3.0 h shaking, 0.5 h settling time].
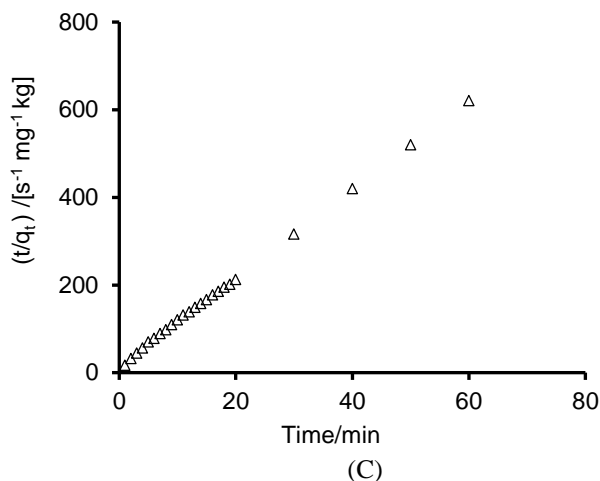

(A)

(B)

Figure 7. Linearized kinetics models for adsorption of Cr(VI) on MP fired at 200 °C at solution temperatures of ambient temperature. (A) pseudo first order kinetics model (B) second order kinetics model (C) pseudo second order kinetics model.

Regression coefficients determined for linearized kinetics models for pseudo first order, second order and pseudo second order are 0.795, 0.920 and 0.999, confirming that the pseudo second order model is the best fitted for the removal of Cu(II). This can be attributed to the presence of two reactive moieties, namely, -OH and -COOH, as stated earlier. The average apparent rate constant, determined at ambient solution temperature for the pseudo second order model is 6.3 kg mg^{-1}min^{-1}, which is higher than reported values of some heavy metal adsorption systems, indicating faster kinetics of Cu(II) on MP [28, 29].

3.7 Applicability of intra-particle diffusion model

The intra-particle model is applied to this system by assuming that the
1) The concentration of Cu(II) in solution is uniform and the amount of Cu(II) adsorbed to the sorbent is zero at $t = 0$;
2) Diffusion is radial with no variation in concentration with angular position;
3) The resistance to transfer in the medium surrounding the particle is significant only in the very early stages of diffusion [30].

Intra-particle diffusion, the diffusion of matter within pores of adsorbent particles, is an important mode of mass transfer that can be considered for an adsorption process. Its linear form can be expressed as

$$\log(q_e) = a \log(t) + \log(k) \tag{7}$$

where t is contact time, k is the intra-particle rate constant and a is a constant to be determined, which is related to the mechanism of sorption [29]. The graphical representation of Equation (7) applied to kinetics data of the Cu(II)- fired peat system is shown in Figure 8. The R^2 value of 0.932 not being close to unity and the small a value of 0.143 indicates that the interaction of Cu(II) on MP does not follow intra-particle diffusion [29], suggesting the possibility of other modes of mass transfer, such as ion exchange and complexation, which were not elaborated in this study.

3.8 Investigation of thermodynamics parameters

The distribution of Cu(II) between the liquid and solid phase is defined by D_α which describes the solid-liquid equilibrium [29]. It can be expressed as

$$D_\alpha = \frac{(C_0 - C_e)\, V}{C_e\, m} \tag{8}$$

where C_0 (mg L^{-1}) is the initial concentration of metal ion in solution phase and C_e (mg L^{-1}) is the equilibrium concentration of metal ion in solution phase, V is the volume of Cu(II) solution (in L) and m is the mass of adsorbent (peat) in kg. The thermodynamics parameters with respect to Cu(II) removal can be described using Equation (9).

$$\ln(D_\alpha) = \frac{\Delta S^0_{ads}}{R} - \frac{\Delta H^0_{ads}}{RT} \tag{9}$$

where ΔS^0_{ads} is the standard entropy of adsorption (J mol^{-1} K^{-1}), ΔH^0_{ads} is the standard enthalpy of adsorption (kJ mol^{-1}), T is the absolute temperature and R is the gas constant.
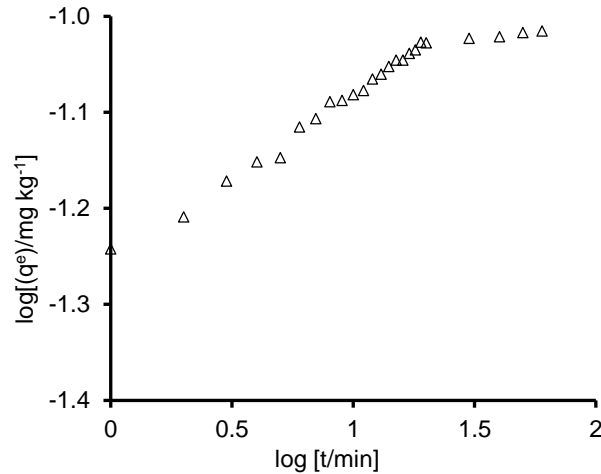

Figure 8. Intra-particle diffusion model of Cr(VI) with peat fired at 200 °C in a solution at ambient temperature [60.0 g of MP, 600.0 mL of Cu(II) solution at moderate stirring].
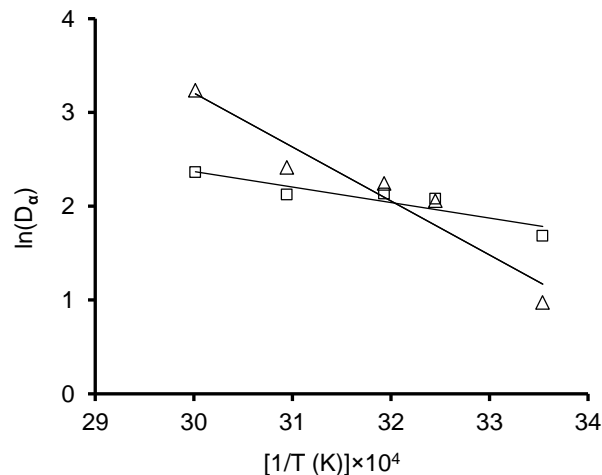

Figure 9. Distribution coefficient of Cu(II) between solid and liquid phase at different temperatures for MP(--□--) (0.60 g) and M-HA (--Δ--) (0.10 g).

Thermodynamics studies were carried out for both MP and M-HA with solutions having initial Cu(II) concentration of 108 mg L^{-1} at different solution temperatures. The standard enthalpy of adsorption (ΔH^0_{ads}) of Cu(II) for M-HA and MP determined from the plot of Equation (9) are 47.9 kJ mol^{-1} and 13.8 kJ mol^{-1}, respectively, while the standard entropy of adsorption (ΔS^0_{ads}) are 170.3

J mol^{-1} K^{-1} and 61.0 J mol^{-1} K^{-1}, respectively (Figure 9). The positive ΔH^0_{ads} for adsorption of Cu(II) on both M-HA and MP indicates the endothermic nature of the process. Higher ΔS^0_{ads} of M-HA - Cu interaction than that of MP-Cu interaction confirms that the affinity of M-HA is more favorable toward Cu(II). Adsorption of Cr(VI) on activated carbon [30] and methylene blue adsorbed on wheat shells [31] also show similar values supporting these findings.

Negative Gibb's free energy values (ΔG^0_{ads}) obtained from Equation (10) indicate the spontaneous nature of the adsorption process (Table 3). The ΔG^0_{ads} for adsorption of Cd(II) on NiO nano-particles and Cr(VI) adsorption on activated carbon are determined to be similar values in support of these findings [29,30].

$$\Delta G^0_{ads} = \Delta H^0_{ads} - T\Delta S^0_{ads} \tag{10}$$

Table 3. Adsorption capacity (qmax) for Cu(II) on different types of peat and humic acid.

Type of adsorbent	Firing temperature/°C	Medium pH	Adsorption capacity/mg kg^{-1}	Reference
Muthurajawela peat (MP) (Sri Lanka)	200	3.5 - 4.0	8.33×10^2	This work
Humic acid extracted from MP (M-HA)	No heat treatment	4.0 - 5.0	6.00×10^3	This work
Peat (Italy)	Oven drying	4.0	3.94×10^4	[19]
	Oven drying	5.0	4.49×10^4	[19]
	Oven drying	6.0	4.97×10^4	[19]
Peat (Ireland)	60	4.0	1.62×10^4	[13]
Humic acid extracted from Ilgin lignite	Oven drying	4.0 - 5.0	2.62×10^4	[28]
Humic acid extracted from Beysehir lignite	Oven drying	4.0 - 5.0	2.8×10^4	[28]
Danish peat	Oven drying	4.0 - .0	3.4×10^4	[13]
Hielongjiang peat	Oven drying	4.0 - 6.0	2.6×10^4	[13]
Eutrophic peat	Oven drying	3.5 - 4.0	2.0×10^4	[15]
Oligotrophic peat	Oven drying	3.5 - 4.0	6.0×10^3	[15]
Humic acid extracted from Canadian sphagnum peat moss	Oven drying	3.5 - 4.0	2.8×10^4	[29]

Table 4. Regression coefficients for linearized kinetics models.

Name of model	Ambient temperature
Pseudo first order	0.795
Second order	0.920
Pseudo second order	0.999

Table 5. Intra-particle diffusion parameters determined from Figure 8 according to Equation (10).

Parameter	Ambient temperature
k (min^{-1})	18
a	0.143
R^2	0.932

Table 6. Gibb's free energy of removal of Cu(II) on M-HA and MP.

Temperature/K	Gibbs's free energy for M-HA - Cu interaction (ΔG^0_{ads})/kJ mol^{-1}	Gibbs's free energy for MP - Cu interaction (ΔG^0_{ads})/kJ mol^{-1}
298.15	-2.90	-4.43
308.15	-4.61	-5.04
313.15	-5.46	-5.34
323.15	-7.16	-5.95
333.15	-8.86	-6.56

4. Conclusions

Batch experiments conducted with aqueous suspensions containing 10.0 mg L^{-1} Cu(II) and peat obtained from Muthurajawela peat land, Sri Lanka (MP), by varying one parameter at a time while keeping others unchanged lead to optimum conditions of 2.5 h shaking time, 1.0 h settling time and 200 °C firing temperature at which 80% removal of Cu(II) is achieved under static conditions. Based on spectroscopic and adsorption equilibrium studies, it is proposed that complexation of –OH and –COOH moieties of compounds present in peat, and ion-exchange be effective modes of mass transfer of Cu(II) from the solution phase to the solid MP matrix. The involvement of both types of reactive moieties for Cu(II) removal is further supported by the pseudo second order kinetics model which leads to a rate constant of 6.3 kg mg^{-1} min^{-1} under ambient solution temperature, at which the diffusion coefficient is determined to be 18 min^{-1} based on the intra-particle diffusion model. The extent of removal of Cu(II) by humic acid extracted from MP (M-HA) is greater by a factor of seven as compared to that of MP, indicating that humic acid present in peat provides a significant contribution toward Cu(II) removal. The standard enthalpy of adsorption (ΔH^0_{ads}) of Cu(II) on M-HA and MP are 47.9 kJ mol^{-1} and 13.8 kJ mol^{-1}, respectively, while the standard entropy of adsorption (ΔS^0_{ads}) are 170.3 J mol^{-1} K^{-1} and 61.0J mol^{-1} K^{-1}, respectively. Higher ΔS^0_{ads} of M-HA - Cu interaction than that of MP - Cu interaction confirms the stronger affinity of the M-HA toward Cu(II). Further, the standard Gibbs free energy values (ΔG^0_{ads}) in the range from -2 kJ mol^{-1} to -8 kJ mol^{-1} indicate spontaneous nature without any induction period.

5. Acknowledgement

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