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Adsorption behaviour of Cr(VI) by Muthurajawela peat

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ABSTRACT

Peat, being a partially decomposed organic material, consists of many organic compounds, such as humic acids and fulvic acids, which contain phenolic, carboxylic acid and amino functionalities, contributing to unique surface characteristics. Firing of peat leads to the loss of organic matter, thus changing the point of zero charge and controlling the extent of adsorption. The change in the initial pH of Cr(VI) solutions does not significantly change the pH of the suspension of Muthurajawela peat (MP) materials and Cr(VI) solutions, maintaining a constant extent of removal. The optimum conditions for the removal of Cr(VI) are 2.0 h shaking time, 1.0 h settling time, 200°C firing temperature and an ambient pH of 3.8–4.2, leading to a high extent of removal of 120 mg kg^{-1}. The sorption of Cr(VI) on MP fulfills the requirements of the Freundlich adsorption model with a high regression coefficient. Further, the sorption of Cr(VI) on peat is a pseudo-second-order process at moderate solution temperatures.

Keywords: Peat; Chromium; Adsorption; Kinetics; Isotherm

1. Introduction

Heavy metals do not undergo biodegradation or decomposition, and they would subsequently enter the food chain causing harmful effects to human health [1]. Effluents released from many industries, such as electroplating, leather tanning, and metal finishing and processing, are contaminated with heavy metal ions and their derivatives [2].

Chemical reduction and precipitation, ion exchange, and adsorption on activated carbon are the most common methods used in removing heavy metal ions [3]. Although activated carbon is an effective adsorbent in removing both metallic and nonmetallic pollutants, high cost associated with its production has promoted more economical adsorbents to be searched upon. High sorption capacity, porosity, high specific surface area and availability in nature are some requirements to be fulfilled by an effective sorbent [4].

Peat, formed by partial decomposition of biological materials, such as grass, shrubs, trees and dead animals under water-logged conditions, is a naturally available and effective adsorbent for heavy metal ions and dyes [5]. It is mainly organic in nature and appears as a brown–black material [6]. There are many reports on the investigation of kinetics and

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equilibrium properties of peat obtained from various geographic locations [4,7–9]. According to many studies, medium pH, which controls the surface characteristics, is probably the most important parameter among other experimental parameters [3,8–11]. Further, competitive adsorption of Pb(II), Cu(II) and Cd (II) on Danish and Heilongjiang (China) peat in both single and multi-solute systems has been found to follow the extent of reaction in the order of Pb(II) > Cu (II) > Cd(II), all of which follow the pseudo-second-order kinetics [1]. Complexation and stability of metal ions, such as Cu(II) and Cd(II), have also been studied with fulvic acid obtained from MP [12]. Investigation of the removal of Cr(VI) from acidic solutions by Romanian *sphagnum* moss peat, and its ability as a reductant have identified a combined mechanism; sorption of anions and reduction of Cr(VI) [2]. The isothermal characteristics of heavy metal ion—peat systems investigated under various experimental conditions indicate that such adsorption systems are not restricted to monolayer adsorption, in contrast to preferential monolayer adsorption of organic dyes [5,13]. Linear and non-linear curve fittings of adsorption isotherms together with error analysis have been the focus of many recent studies of heavy metal ion—peat systems to identify the most suitable adsorption pattern [14,15].

As the adsorbent (peat) does not represent a homogeneous system, the optimization of process and experimental parameters is essentially a critical initial step of adsorption research involving peat. Once the set of experimental conditions is properly optimized, the extent of sorption leads to the maximum efficiency within a reasonable period of time. Further, isotherm studies, conducted under adsorption equilibrium conditions, provide fundamental physicochemical data for the prediction of sorption mechanisms. In this context, the aim of this study was to characterize the peat material using thermal gravimetric analysis (TGA), surface titrations and Fourier transform infrared spectroscopy (FTIR), and to investigate adsorption characteristics of Cr(VI) species on peat material obtained from Muthurajawela (MP), the main peat deposit in Sri Lanka. Process parameters, which directly affect the removal of metal ions, such as shaking time (agitation time), settling time (resting time after agitation) and the temperature at which MP is pre-thermally before adsorption studies (firing temperature), were optimized in this study followed by equilibrium and kinetics studies. A comparative study of the differences between anionic and cationic chromium species was also performed. It should be stressed that MP is an ill-studied system as far as the heavy metal-ion removal is considered.

2. Materials and methods

2.1. Preparation of samples

Representative samples of MP were taken at 7´4´ 32.5 N, 79´51´ 58.2 E geographical location. They were allowed to air-dry for a few weeks until there was no further mass loss. The randomly obtained air-dried samples of peat were then ground well to obtain the particles of diameter <1 mm, followed by manual homogenization. These samples were thermally treated for 4.0 h at predetermined temperatures from 100 to 700˚C with 100˚C intervals.

2.2. Materials

Analytical grade $K_2Cr_2O_7$ and $Cr(NO)_3$, both of which were purchased from BDH chemicals, were used to prepare standard solutions for all experiments. Analytical grade $NaNO_3$ (Panreac) was used to prepare solutions of different concentrations to conduct surface titrations. Na_2CO_3 (Panreac) was used as a primary standard to standardize the HNO_3 (SCP) solutions.

2.3. Characterization

2.3.1. Thermal analysis (TGA-DSC)

Thermogravimetric analysis was carried out for raw samples of MP in order to quantify the organic matter content. Heat flow and mass of residue were measured within the temperature range from 25 to 900˚C.

2.3.2. pH (point of zero charge—pH_{pzc})

Experiments of surface titrations were carried out to investigate the surface charge of peat materials. For surface titrations, a sample of 0.75 g of MP which was stirred with 125 cm^3 of 0.10 mol dm^{-3} $NaNO_3$ solution was used. Then, it was titrated up to the pH of 10.0 with NaOH solution (0.0898 mol dm^{-3}, standardized with the secondary-standard HNO_3 acid of 0.0940 mol dm^{-3} which was standardized with a primary-standard Na_2CO_3 solution of 0.100 mol dm^{-3}). This experiment was repeated for $NaNO_3$ solutions of concentrations 0.010 mol dm^{-3} and 0.0010 mol dm^{-3}. Changes in the pH of peat suspensions were recorded when the NaOH solution was added drop wise. Surface charge density–pH curves were then constructed in order to determine the point of zero charge. The entire experiment was repeated for MP thermally treated at 200 and 400˚C, and the point of zero charge was determined for each sample.

2.3.3. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of MP thermally treated at 200˚C and thermally treated peat after individual treatment with Cr(III) and Cr(VI) solutions of 1,000 mg L^{-1} under optimum conditions were recorded on Thermo Nicolet Model-Avatar 320 FTIR spectrophotometer. FTIR spectra obtained were used for structural determination.

2.4. Desorption components from thermally treated peat

Desorption components of thermally treated MP fired at different temperatures were analysed by the treatment of 25.0 g of MP with 400 cm^3 of distilled water. Anions (Cl^-, SO_4^{2-}, PO_4^{3-} and NO_3^-) and metal ions in the supernatant were analysed using standard methods.

The Carbolite CTF 12/100/900 tube furnace was used to heat peat samples. Spectro-Electronic M Series atomic-absorption spectrophotometer was used to measure the metal ion concentrations of all solutions. Concentrations of NO_3^- and Cl^- were determined using respective ion-selective electrodes (Jenway 3205). Determination of PO_4^{3-} was conducted using the Vanadomolybdate method, and measurements were taken on UV/vis spectrophotometer (Shimadzu-1800UV). The concentration of SO_4^{2-} was determined with the aid of turbidity measurements using turbidity meter (HACH 2100p).

2.5. Adsorption

2.5.1. Optimization parameters

The standard solutions of each metal ion solution of 10.0 mg L^{-1} concentration were thoroughly mixed with peat in 1:10 (W/V) ratio for optimization experiments. Firing temperature, shaking time and settling time were optimized in order to study the removal efficiency of Cr(III) and Cr(VI) species. The effect of pH of the solutions on the extent of removal was studied within 2–10 pH range under the optimized conditions. Removal efficiency was calculated using the following equation:

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

where C_0 is the initial concentration of metal ion in solution phase and C_f is the final concentration of metal ion in solution phase.

2.5.2. Isotherms

Metal ions of different concentrations were used for the adsorption study, under optimized conditions. The extent of adsorption was then calculated and used for testing the validity of adsorption isotherms.

The Freundlich isotherm model is given by:

$$q_e = k_F C_e^n \tag{2}$$

where C_e is the concentration of metal ion in solution phase at equilibrium (mg dm^{-3}) and q_e is the amount adsorbed at equilibrium (mg kg^{-1}). The linearized form of the above equation can be represented as:

$$\ln q_e = n \ln C_e + \ln k_F \tag{3}$$

where n and k_F are Freundlich isotherm constants.

2.5.3. Kinetics studies

Kinetics models, such as first-order, pseudo-first-order and pseudo-second-order were tested for the removal of Cr(VI) on peat thermally treated at 200˚C. For kinetics studies, aliquots of 600 cm^3 solutions of Cr(VI) of 10.0 mg L^{-1} concentration were treated with 60.0 g of thermally treated MP at 200˚C. While the solution was being stirred, 10.00 cm^3 aliquots of the solution were withdrawn at every one-minute interval up to 6 min. Then, a sample was withdrawn after 60 min when the solution reached equilibrium. The same procedure was repeated in solutions of different temperatures.

3. Results and discussion

3.1. Characterization

3.1.1. Thermal analyses (TGA-DSC)

The mass loss of a representative sample of MP together with the extent of heat released when the sample is heated from ambient temperature up to 900˚C is shown in Fig. 1. Negative heat flow recorded up to about 100˚C is attributed for the removal of moisture present in peat, which is an endothermic process. Beyond this temperature, heat flow becomes positive owing to the combustion of organic matter present in peat, an exothermic process. Heat flow gradually increases up to 300˚C and levels off up to 425˚C, indicating the completion of combustion of the organic matter. After this temperature, the heat flow is decreased again and levelled off at a lower positive

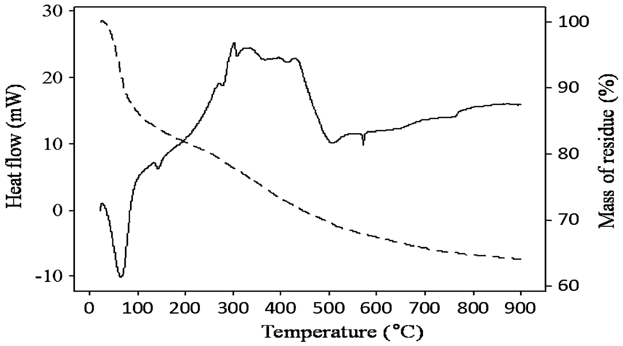

Fig. 1. Variation of mass of MP (- - -) and heat flow (—) upon firing a representative sample of MP up to 900˚C.

value. This could be attributed to the combustion of matter which is not burnt up to 425˚C, and phase transitions of clay minerals which require higher firing temperatures. It should also be noted that the mass is continuously lost during firing up to 900˚C. Reported data of organic matter content as %C are shown in Table 1. The organic matter content of MP is determined to be 37% according to mass loss measurements, which is comparable to peat in many regions.

3.1.2. pH (point of zero charge pH_{pzc})

The pH at the point of zero charge (pH_{pzc}) is a valuable index for adsorption studies because Coulombic attraction and ion-exchange, two main modes of mass transfer of ionic species from the solution phase to the peat matrix, highly depend on the surface charge which thus influences the extent of adsorption of charged species. The pH_{pzc} for MP in its natural form, thermally treated at 200˚C and thermally treated at 400˚C, determined by estimating the point of intersection of surface charge density—medium pH curves constructed in solutions of different ionic strengths, are 3.8, 4.2 and 8.5, respectively (Fig. 2). The pH_{pzc} obtained for MP in its natural form is comparable with what has been reported for peat in Thailand and Malaysia [9,16], while it is little higher as compared to that of Peat in Brunei Daruussalam [15]. The increase in pH_{pzc} with firing temperature can be attributed to the loss of organic matter, in particular, compounds containing phenolic and carboxylic groups. These compounds, which would undergo combustion during firing, are responsible to create negative charges on the surface of peat materials. Therefore, higher medium pH (higher concentration of OH^- ions) would be required to maintain the surface neutrality of thermally

Table 1
Organic matter content of different peat soils

Type of peat soil	%C	Refs.
Danish peat	45	[1]
Heilongjiang	33	[1]
Brazil peat	38	[2]
Ayer Bobi peat	42	[9]
Bacho peat	18	[9]
Muthurajawela peat (MP)	37	This work

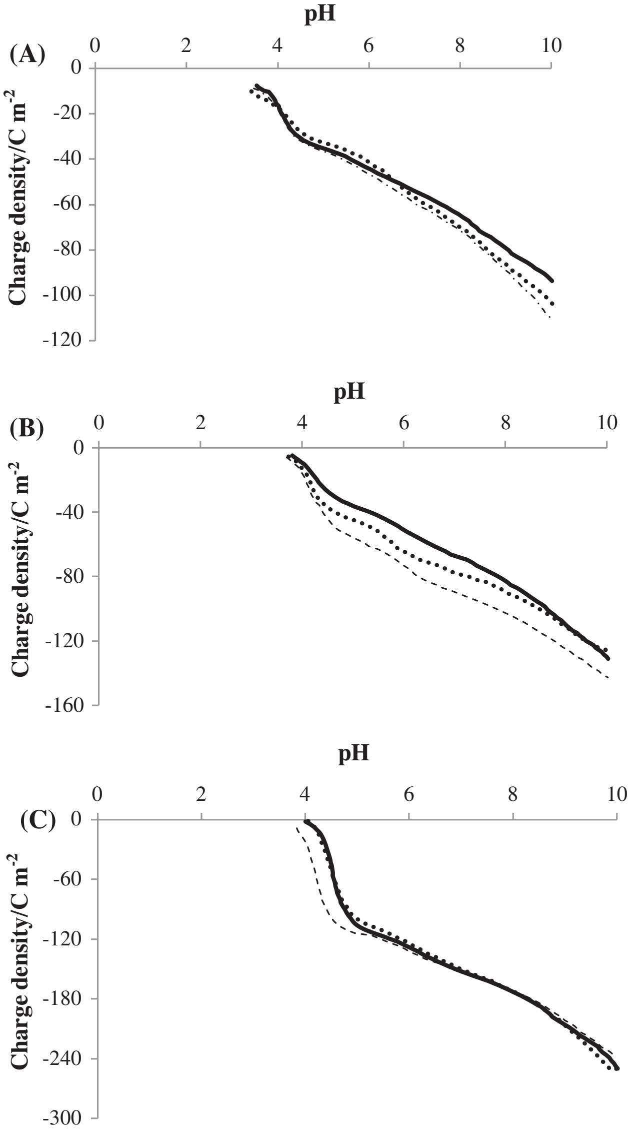

Fig. 2. Surface titration curves of peat suspensions, plotted as variation of surface charge density with pH for (A) unthermally treated peat, (B) peat thermally treated at 200˚C and (C) peat thermally treated at 400˚C. Ionic strengths are 0.10 mol dm^{-3} (- - -), 0.01 mol dm^{-3} (—) and 0.001 mol dm^{-3} (….) with respect to $NaNO_3$ solutions.

treated peat at higher temperatures, thus having a higher pH_{pzc}.

3.1.3. Fourier transform infrared spectroscopy (FTIR)

Fig. 3 shows the FTIR spectra of MP thermally treated at 200°C before and after treatment with Cr(III) and Cr(VI). The characteristic features of FTIR spectra of MP thermally treated at 200°C indicate the presence of C=O in phenolic groups and carboxylic groups (broad peak from 3,000 to 3,600 cm^{-1}), C=C (1,655 cm^{-1}), C–C (1,119 and 1,134 cm^{-1}), C–H (540 cm^{-1}) and nitro groups (1,385 cm^{-1}). The spectral peaks of MP treated with Cr(III) and Cr(VI) followed by firing at 200°C have shifted to the higher wave number direction indicating the influence of binding of chromium species.

3.2. Desorption components from thermally treated peat

As the MP deposit is close to the ocean, it would have been contaminated with seawater, and consequently, it is expected that MP consists of anions, which are usually rich in the ocean. These ions are probably not chemically bonded to the peat matrix, and hence, thorough mixing of MP with water is able to transfer such loosely bound ions into water. Table 2 indicates the concentration of common ions that have been desorbed during the treatment of peat, thermally treated at different temperatures, with deionized water. Higher values of chloride and sulphate concentrations can be attributed to the impact of Dutch canal which flows through the peat deposit into the sea [17].

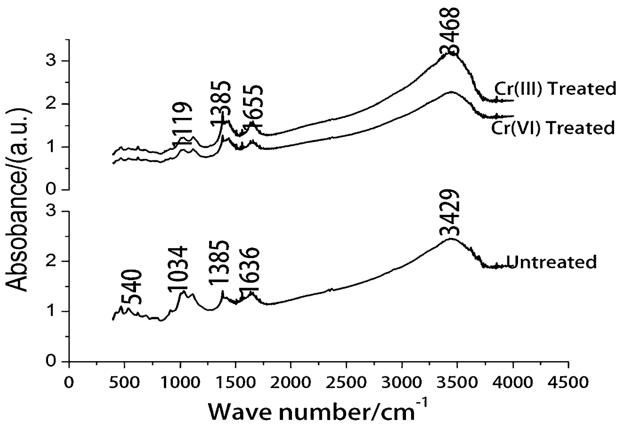

Fig. 3. FTIR spectra of MP thermally treated at 200°C (bottom); MP thermally treated at 200°C followed by treatment with Cr(III) and Cr(VI) (top) (5.00 g peat, 50.0 cm^3 solution, 2.0 h shaking, 1.5 h settling, 1,000 mg L^{-1}).

The concentrations of all anionic constituents (Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) generally decrease with an increase in the firing temperature of peat (Table 2). This could be due to the fact that these anions occupy lattice sites of minerals present in peat during treatment, and therefore, they are not easily desorbed. A similar trend was observed in desorbed solutions of montmorillonite clay after treatment with a solution containing Cl^- and SO_4^{2-} to simulate the oceanic environment, supporting the above fact. On the other hand, concentrations of heavy metal ions, such as Cd (II), Cr(III), Cu(II), Ni(II) and Pb(II), are negligible in the desorbed solution of peat when compared to Zn (II), which could be present naturally. The concentration of Zn(II) in the desorbed solution also decreases with the firing temperature. Attempts were not taken to determine the concentrations of cations, such as Na^+, K^+, Mg^{2+} and Ca^{2+}, in this study due to their harmless nature to the environment/eco system.

3.3. Adsorption

3.3.1. Optimization parameters

Optimization is a major requirement for pollutant removal studies because it would lead to the maximum efficiency within a short period of time. The extent of removal of Cr(VI), determined by the treatment of 5.00 g ($d < 1$ mm) of peat pre-thermally treated at temperatures up to 700°C with 50.0 cm^3 of 10.0 mg L^{-1} Cr(VI) solution at an ambient pH, indicates that the firing temperature of 200°C is the optimum for Cr(VI) removal. At this temperature, the best adsorption capacity with the minimum turbidity was observed. High removal efficiency of MP thermally treated at 200°C, as compared to its natural form, is probably due to expansion and opening of adsorption sites/pores on the peat surface. At an ambient pH of 3.8, the surface of peat thermally treated at 200°C is positively charged, because $pH < pH_{pzc}$. This promotes the Coulombic attraction of Cr(VI) species towards the surface of MP particles, thereby removing chromium species from solution. In addition to the transfer of Cr(VI) to the MP surface, Cr(VI) which is present as $HCrO_4^-$ at low ambient pH undergoes reduction according to the following reaction due to the strong oxidizing nature of $HCrO_4^-$ [2].

$$HCrO_4^-(aq) + 7H_3O^+(aq) + 3e \rightarrow Cr^{3+}(aq) + 11H_2O \tag{4}$$

The high-positive standard reduction potential (1.20 V) of the above reaction provides strong evidence for the

Table 2
Concentration of ionic desorption components of peat thermally treated at different temperatures (initial mass of MP = 25.0 g, volume of solution = 400.0 cm^3)

	Concentration of ions (mg L^{-1})				
Firing temperature (℃)	Cl^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	Zn(II)
Unfired	1,058	18	1,838	7	2.10
100	1,712	24	2,700	6	2.52
300	545	7	3,978	2	2.10
600	5	2	2,652	8	0.40
900	4	1	327	7	0.01

reaction to proceed, which would couple with the oxidation of humic substances present in peat [18]. When the above reaction proceeds, the medium pH would start to increase. When the medium pH becomes greater than pH$_{pzc}$, the particles of MP would bear a negative charge, thus promoting Cr(III) species to be adsorbed through Coulombic attraction. High initial removal of Cr(VI) species with MP thermally treated at 200℃ is thus explained.

When a solution of only Cr(III) is treated with MP under ambient pH conditions, the above reaction would not take place, and hence, no redox chemistry would occur. As the surface of MP thermally treated at 200℃ at ambient pH is positively charged, Cr(III) would not be attracted to the MP surface, and hence, the extent of removal of Cr(III) by MP thermally treated at 200℃ is lower than that of Cr(VI). Nevertheless, the observed value of 50% removal as compared to 60% for Cr(VI) could be explained due to a complexation mechanism between Cr(III) and organic functionalities of humic substances, and an ion-exchange mechanism involving carboxyl groups as shown below [19].

$$3(\mathrm{COOH})(\mathrm{aq}) + \mathrm{Cr}^{3+}(\mathrm{aq}) \rightleftarrows (\mathrm{COO})_3\mathrm{Cr}(\mathrm{aq}) + 3\mathrm{H}^+(\mathrm{aq}) \tag{5}$$

$$(\mathrm{COOH})(\mathrm{aq}) + \mathrm{CrOH}^{2+}(\mathrm{aq}) \rightleftarrows (\mathrm{COO})_2\mathrm{CrOH}(\mathrm{aq}) + 2\mathrm{H}^+(\mathrm{aq}) \tag{6}$$

$$(\mathrm{COOH})(\mathrm{aq}) + \mathrm{CrOH}_2^+(\mathrm{aq}) \rightleftarrows (\mathrm{COO})\mathrm{Cr}(\mathrm{OH})_2(\mathrm{aq}) + \mathrm{H}^+(\mathrm{aq}) \tag{7}$$

It should however be stressed that firing temperatures higher than 200℃ would allow the combustion of humic substances and other organic compounds having functionalities responsible for the removal of either Cr(VI) or Cr(III), resulting in lower chromium removal.

It is observed that the pH of the suspension of peat thermally treated at 200℃ and Cr(VI) solutions of different initial pH from 2.6 to10.0 is levelled off to about 4.2, the pH$_{pzc}$ of peat, with the exception of the extremely high initial pH of 10.0. Thus, it is proposed that the reduction of $HCrO_4^-$ species forming Cr(III) followed by its adsorption occurs regardless of the initial pH, maintaining a constant extent of removal, as observed in Fig. 4. The extent of removal at the initial pH of 10.0 is probably due to an ion-exchange mechanism between Cr(VI) species and negatively charged surface species as the reduction of Cr(VI) is not possible at higher pH. On the other hand, increase in the extent of removal from Cr(III) solution increases at high initial pH, probably due to precipitation of its hydroxide (Fig. 4).

In addition to the above facts, optimization of shaking and settling times for the most efficient removal of Cr(VI), determined using 10.0 mg L^{-1} solution within a broad range of shaking and settling time periods, leads to 120 and 90 min, respectively.

3.3.2. Isotherms

The amount of Cr(VI) adsorbed on MP thermally treated at 200℃ continuously increases when the initial concentration increases even up to a concentration as high as 4,000 mg L^{-1} as shown in Fig. 5, in contrast

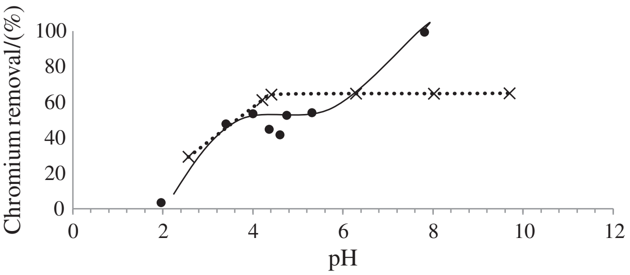

Fig. 4. Effect of initial solution pH on adsorption of Cr(VI) (··×··) and Cr(III) (-●-) on peat thermally treated at 200℃ (5.00 g peat, 50.0 cm^3 solutions, 2.0 h shaking, 1.5 h settling).

to dye adsorption under similar circumstances [5]. This clearly explains the strong affinity of peat towards Cr(VI). Although the extent of removal increases with concentration, the percentage removal of Cr(VI) becomes constant after an initial concentration of 2,000 mg L^{-1} as shown in Fig. 6, indicating that the amount of chromium adsorbed and the initial concentration show a linear variation beyond this concentration up to 4,000 mg L^{-1}, as observed in Fig. 5.

Equilibrium isotherms show the relationship between the amount of material adsorbed as a function of the equilibrium-adsorbate concentration. As the MP surface does not become saturated as observed in Fig. 5, the Freundlich adsorption isotherm, which accounts for multi-layer adsorption, would be more suitable. This isotherm model when plotted as $\ln q_e$ vs. $\ln C_e$ results in a regression coefficient of 0.955, suggesting the validity of the Freundlich isotherm for the system of peat-Cr(VI) solution (Fig. 7). Further, the isotherm constants n and k_F, determined from the isotherm plot, are 0.525 and 66, respectively. The n value between 0.0 and 1.0 indicates favourable adsorption, while the relatively high k_F value suggests the availability of a large number of active sites. This observation is further evidenced by reports on the validity of the Fruendlich adsorption isotherm for Cr(VI) on different adsorbents [10]. For instance, Cr(VI) adsorbed on thermally treated brick clay particles has resulted in 0.95 and 4.58 for n and k_F, respectively [20].

In checking the validity of the Freundlich isotherm, the difference between the initial amount of Cr(VI) and what is left in solution after the establishment of equilibrium was used as a measure of the amount adsorbed. However, it does not mean that all the materials transferred to the solid MP phase localize at the surface forming a multilayer. After completion of the monolayer, the species adsorbed could be transferred to the bulk of the material through many mass transfer processes, as explained elsewhere, allowing more adsorbate species to be adsorbed [21]. This could be viewed as a continuous increase (after the completion of a monolayer) in the amount of Cr(VI) removed from solution as observed in Fig. 5.

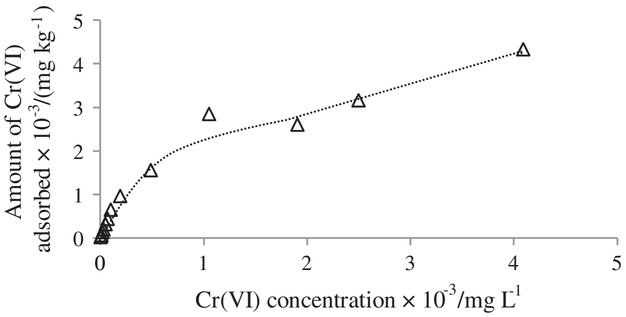

Fig. 5. Extent of Cr(VI) adsorbed on MP under optimum conditions (5.00 g peat, 50.0 cm^3 solution, 2.0 h shaking, 1.5 h settling).

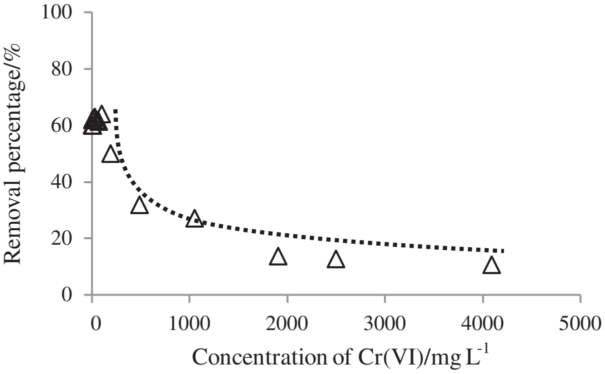

Fig. 6. Removal percentage of Cr(VI) on peat under optimum conditions (5.00 g peat, 50.0 cm^3 solution, 2.0 h shaking, 1.5 h settling).

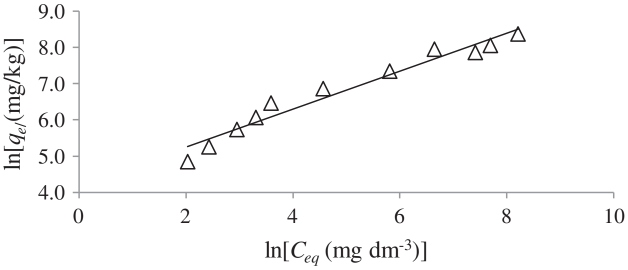

Fig. 7. Freundlich isotherm model for adsorption of Cr(VI) on MP thermally treated at 200°C (5.00 g peat, 50.0 cm^3 Cr(VI) solution, 2.0 h shaking, 1.5 h settling).

3.3.3. Kinetics studies

Adsorption systems involving natural adsorbents are usually characterized by pseudo-first-order, second-order and pseudo-second-order kinetics models. The linearized forms of the above models are given by:

$$\log(q_e - q_t) = -\frac{k'}{2.303}t + \log(q_e) \tag{8}$$

$$\frac{1}{q_e - q_t} = k't + \frac{1}{q_e} \tag{9}$$

and

$$\frac{t}{q_t} = \frac{1}{q_e}t + \frac{1}{k'q_e^2} \qquad (10),$$

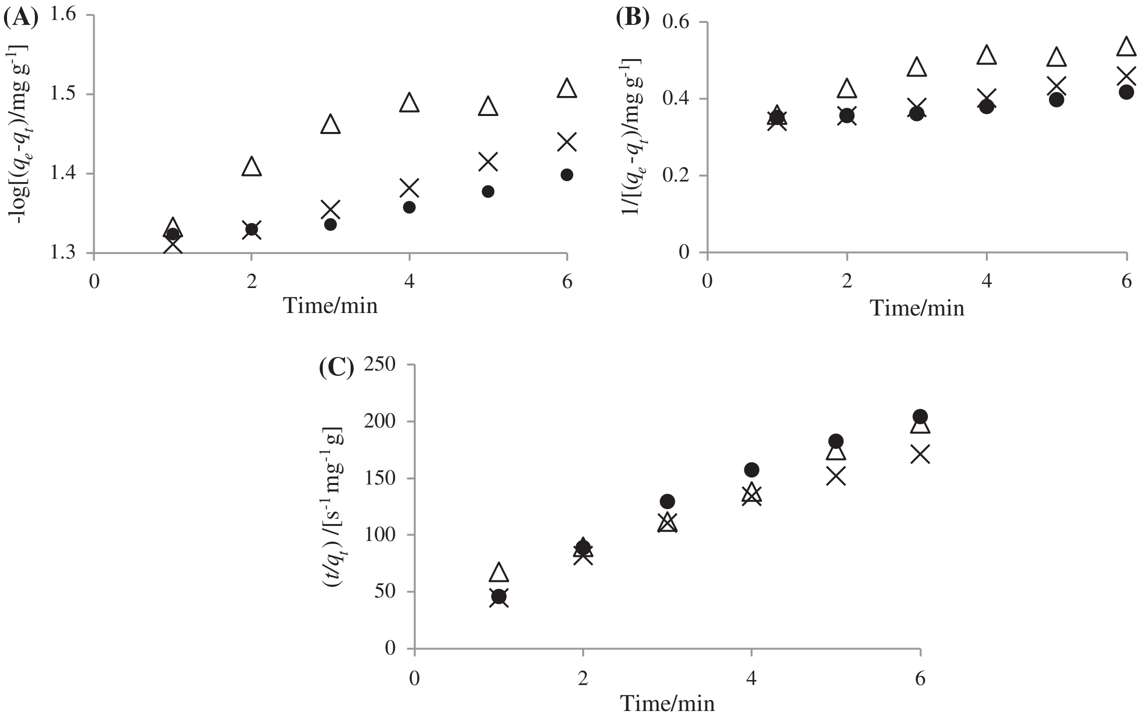

Fig. 8. Linearized kinetics models for adsorption of Cr(VI) on MP thermally treated at 200˚C at different reaction temperatures: ambient temperature (Δ), 45˚C (●) and 60˚C (×). (A) pseudo-first-order kinetics model, (B) second-order kinetics model and (C) pseudo-second-order kinetics model (60.0 g of MP, 600.0 cm^3 of Cr(VI) solution at moderate stirring).

respectively, where k' is the apparent rate constant, t is the contact time and q_e and q_t are the masses of Cr (VI) sorbed by unit mass of sorbent at equilibrium and at time t, respectively. As q_t is more conveniently expressed in mg of Cr(VI) adsorbed by 1.00 g of peat thermally treated at 200˚C, the apparent rate constant k' is estimated in s^{-1} for first-order reactions and g mg^{-1} s^{-1} for pseudo-second-order reactions. In order to apply the pseudo-order conditions, one of the reactants should be maintained at a higher concentration, assuming that the change in the concentration of this species is not significant as compared to that of the other reactant. In the kinetics studies, the initial concentration of Cr(VI) species was made at 10 mg L^{-1} and the measurement was taken within the initial six-minute period, so that the concentration of the Cr(VI) at the end of the period was greater than 75% of the initial value. Therefore, it is reasonable to assume that the pseudo-order condition can be applied with respect to Cr(VI) species.

Plots of the kinetics models constructed for solutions of Cr(VI) at ambient temperature, 45 and 60˚C are shown in Fig. 8. Regression coefficients of the three kinetics models at each solution temperature are given in Table 3. Based on the values estimated, the pseudo-second-order kinetics model is well in agreement with the adsorption system under investigation at an ambient temperature and at 45˚C with the rate constants of 19.7 g mg^{-1} s^{-1} and 40.5 g mg^{-1} s^{-1}, respectively. Regression analysis of the kinetics models for sorption at 60˚C suggests that it is difficult to propose one model. A similar trend of having increased R^2 values of the pseudo-second-order model at warmer temperatures has been reported for the sorption of Cr(VI) on activated carbon [10].

These results can be interpreted by considering the presence of two types of functional groups: carboxylic acid and phenolic acid, which would form complexes with Cr(III) upon the reduction of Cr(VI). When the solution temperature is raised to 60˚C, the processes, such as increase in ionization of functional groups,

Table 3
Regression coefficients for kinetics models for sorption of Cr(VI) on peat thermally treated at 200˚C

Kinetics model	Ambient temperature	45˚C	60˚C
Pseudo-first-order	0.841	0.946	0.993
Second-order	0.869	0.939	0.987
Pseudo-second-order	0.992	0.980	0.979

increase in entropy, expansion of pores and increase in kinetic energy of reaction species, would make the situation different from that at lower temperatures.

4. Conclusion

Thermal analysis of peat indicates the combustion of organic functionalities of the compounds present in peat. The point of zero charge (pH_{pzc}) in its natural form, thermally treated at 200˚C and thermally treated at 400˚C are 3.8, 4.2 and 8.0, respectively. The optimum firing temperature of peat for the most efficient removal and the lowest turbidity is determined to be 200˚C. $HCrO_4^-$, the most predominant species, undergoes reduction forming Cr(III) followed by its adsorption through Coulombic attraction to the surface of and subsequent complexation with carboxylic and phenolic functional groups. The extent of removal of Cr(VI) is therefore significantly decreased at higher temperatures due to the loss of organic matter. On the other hand, the extent of removal of initially present Cr(III) thermally treated at 200˚C is much less than that of Cr(VI) at an ambient pH as medium $pH < pH_{pzc}$. The sorption reaction of Cr(VI) by MP follows the Freundlich adsorption isotherm and pseudo-second-order kinetics with a high average rate constant of $30\ g\ mg^{-1}\ s^{-1}$. The validity of the pseudo-second-order kinetics indicates that the rate of sorption is controlled by two types of reactive functional groups of peat materials, mainly carboxylic and phenolic groups. The findings of this study explain the affinity of MP for Cr(VI) species, which would pave the way toward the design of treatment plants for industrial effluents containing such species.

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