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Enhanced removal of Ni(II) by acetic acid-modified peat

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ABSTRACT

X-ray fluorescence (XRF) spectroscopy and Fourier transform infrared (FTIR) spectroscopy of peat obtained from the Muthurajawela deposit in Sri Lanka indicate the presence of K, Ca, Ti, Fe and S, and –OH and –COOH functional groups. X-ray diffraction (XRD) patterns obtained for both raw peat and acetic acid modified peat (AAMP) provide evidence for the presence of crystalline substances along with amorphous matter. Acid treatment of peat improves the extent of Ni(II) removal, and more importantly, AAMP shows a remarkable enhancement together with low turbidity of the resulting suspension. Scanning electron microscopy (SEM) indicates that adsorption of Ni(II) on AAMP leads to the reduction of its pore structure, confirming the adsorption of Ni(II) on the surface of AAMP. The optimum values of the concentration of acetic acid, dosage, shaking time, settling time and pH for Ni(II) – peat interaction are 0.01 mol dm^{-3}, 5.00 g, 45 min, 20 min and 5–6, respectively. The adsorption capacity of AAMP toward Ni(II) under the optimized conditions is 6.24×10^2 mg kg^{-1}. The sorption of Ni(II) on AAMP obeys the Freundlich adsorption isotherm, following pseudo second order kinetics. Ni(II) adsorbed on AAMP particles would not leach Ni(II) significantly under ambient conditions.

Keywords: Acetic acid modified peat; Adsorption isotherm; Kinetics; Nickel; Surface modification; Desorption

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1. Introduction

Water, abundantly available on the Earth, is essentially required for all living organisms. However, only about 0.3% of fresh water is found as surface water of lakes, rivers and swamps [1], and therefore, it is important to protect water sources, without further pollution. Environmental pollution occurs on land, in air and in water, and it has already become a severe global problem. Among many types of pollutants, heavy metals released from various industries are considered as the most hazardous substances [2]. They are subject to neither decomposition nor degradation, thereby accumulating in water bodies causing water pollution. This leads to bioaccumulation of heavy metals in food chains [3].

Most heavy metals are stable at elevated temperatures and pressures due to their high melting points, and most are good conductors. Due to the presence of unpaired *d* electrons, they show magnetic properties, and some metals form paramagnetic compounds [4]. Therefore, heavy metals are widely used in many industries due to the desirable characteristics mentioned earlier. Among different heavy metals, Ni(II) is a heavily used industrial metal, which shows high ductility, good thermal conductivity, moderate strength and hardness. It is considered as a corrosion resistant metal, and about 6% of the world nickel production is used for corrosion resistant nickel plating. This metal is used in many industrial and consumer products, including stainless

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steel magnets, rechargeable batteries, electric guitar strings, microphone capsules and alloys. Nickel is used as a binder in the cemented tungsten carbide in hard metal industry. Nickel sulfide fumes and dust are believed carcinogenic, and nickel carbonyl is an extremely toxic gas [5].

Chemical methods used for the removal of heavy metals from contaminated water include precipitation, oxidation and reduction, coagulation and flocculation, and ion exchange [6]. Physical methods are membrane-filtration, electrodialysis and adsorption. In biological methods, living organisms, such as plants, bacteria and fungi are used in treatment processes. Some examples for biological methods are biosorption, activated sludge process, biofilters and anaerobic digestion [7]. Adsorption, among other metal removal methods, has taken the lead due to many advantages, such as selectivity, specificity, ease of operation, high removal capacity and economic factors [6,8]. Another unique advantage of adsorption is that the adsorbents are natural and environmentally friendly to trap toxic heavy metal ions. Adsorption depends on many factors, such as temperature, pressure, surface area and activation of adsorbent. Activated carbon, zeolites, clay, rice husk, coir dust, saw dust, peat and some agricultural waste products are commonly used adsorbents [9].

Several functionalities present in natural sorbents are, carboxyl, hydroxyl, amine and phosphoryl groups, which are involved in bonding of heavy metal ions [10]. Even though several types of biosorbents are available, the presence of functional groups with bonding abilities does not always assure biosorption due to steric factors [11]. Sorption capacity thus depends on the type of adsorbent and the nature of wastewater treated.

Peat, among many natural adsorbents, has been used as an effective adsorbent for metal ions and their compounds [12]. Further, peat and its modified forms have cation exchange properties [13]. Peat forms largely from inhibited decomposition of materials, such as grass, shrubs and dead bodies, under water-logged conditions. Peat is the earliest stage of the formation of coal, and its chemical composition varies widely with geographical region, age and within individual deposits due to chemical reactions resulting in its formation [12]. The majority of the world's peat lands occur in boreal and temperate zones, where high precipitation with low temperature climatic conditions is available [13]. Tropical regions also have good conditions, which enable peat formation under high precipitation and high temperature [14]. Muthurajawela in Sri Lanka is an example for a tropical peat land. In such peat lands, the water table rises above the surface due to the high rainfall in the wet season. The water level drops below the soil surface during drier months of the year creating conditions that would promote the natural decomposition of organic matter and formation of acidic soil [15]. However, all peat deposits show a very low growth rate of about 1 mm/y [16].

The adsorption ability of peat is due to the presence of humic acid, fulvic acid and cellulose. Humic acid and fulvic acid contain carboxylic and phenolic groups, while cellulose is a complex structure. Thus, peat shows affinity toward metal ions. The objective of this research was to investigate the effect of chemical modification, using acid treatment of peat obtained from Muthurajawela, Sri Lanka, on the removal of Ni(II) from synthetic effluents. Optimization of experimental parameters, such as concentration of acid for treatment of peat, adsorbent dosage, stirring time, settling time and solution pH, would be needed to obtain the most efficient removal conditions. Adsorption isotherm models, such as Langmuir and Freundlich, lead to the identification of the type of adsorption, surface properties and to find the adsorption capacities of the adsorbent selected. Further, adsorption kinetics of the system can be understood using kinetics models and diffusion models, and the validity of different mass transfer modes can be studied using the intra-particle diffusion model. Surface charge and surface area of the adsorbent were also determined, as they also provide information on the adsorption process.

2. Materials and methods

2.1. Materials

Standard solutions of Ni(II) were prepared using analytical grade $NiSO_4$ (BDH Chemicals). Solutions of different initial pH values were prepared using HNO_3 and NaOH solutions. Solutions of $NaNO_3$were used for the investigation of the point of zero charge. Samples of Muthurajawela peat (MP) were taken from *7′ 4′ 32.5* N and *79′ 51′ 58.2 E* geographical locations. Solutions of HNO_3, HCl, CH_3COOH and $H_2C_2O_4$ of different concentrations were prepared to treat peat particles. A fraction of peat samples was heated up to 200°C before treatment with HNO_3 and HCl for the maximum absorbance of cations according to previous findings [17]. All the experiments were conducted under static conditions, with acid treated peat particles of diameter (d) <1.0 mm, followed by manual homogenization. Powdered acid treated peat particles of $d < 0.063$ mm were used for X-ray diffraction (XRD), X-ray fluorescence (XRF) spectroscopy, Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). Methylene blue was used to determine the surface area of acetic acid modified peat (AAMP).

2.2. Instrumentation

Peat samples were fired using Carbolite CTF 12/100/900 tube furnace. Turbidity of each solution was measured using a turbidity meter (HF Scientific Inc., Model DRT15CE). The total concentration of Ni(II) in all solutions was determined using Spectro-Electronic M Series atomic absorption spectrophotometer (AAS). XRD patterns of peat samples were recorded on a Siemens X-ray diffractometer (Model-D50000) and XRF studies were conducted using X-ray fluorescence spectrophotometer (Fischerscope Model-DF500FG-456). FTIR spectra were recorded on IR Prestige-21 (SHIMADZU) FTIR spectrophotometer and SEM images were obtained from Scanning Electron Microscope, ZEISS EVO|LS15.

2.3. Research Design

2.3.1. Chemical modification of peat

2.3.1.1. Sample preparation

A bulk sample of peat was crushed and mixed well to form a homogeneous mixture. Raw peat samples from the homogenized mixture were separated into particles of $d < 1.0$ mm using a set of sieves. Thereafter, one part of the raw peat sample was heated at 200°C for a period of 4.0 h, and the other part was taken as raw peat. Raw peat samples were separately treated with different acid solutions (HNO_3, HCl, CH_3COOH and $H_2C_2O_4$) of concentrations ranging from 0.01 to 0.20 mol dm^{-3} (mass of peat:acid volume = 1:10 ratio, 2.0 h shaking time and 2.0 h settling time). Thereafter, the treated peat samples were washed with distilled water until the pH was in the range 4.0–5.0, and allowed to air dry. The removal percentage of Ni(II) was then determined for both treated and raw peat. Finally, acetic acid modified peat (AAMP) samples (0.01 mol dm^{-3}) were used in further characterization due to the best performance of acetic acid with regard to both efficiency of removal and the level of turbidity.

2.3.2. Characterization of acetic acid treated peat

2.3.2.1. XRF and XRD analysis

For XRF and XRD analysis, 2000 mg L^{-1} Ni(II) solutions were treated with AAMP samples under optimized conditions. Each suspension was filtered, and samples of Ni(II)–sorbed AAMP were air dried. Thereafter, dried samples and unmodified peat samples were crushed to obtain particles of size $d < 0.063$ mm for XRF and XRD analysis.

2.3.2.2. FTIR analysis

Pellets were prepared for FTIR spectroscopic analysis by mixing fused KBr with powdered samples of raw peat, AAMP and Ni(II) sorbed AAMP, of particle size $d < 0.063$ mm in 30:1 ratio.

2.3.2.3. Characterization of surface sites

Surface acidic sites and surface basic sites were determined using the Boehm titration method for both raw and AAMP. For this, a sample of 0.25 g of each raw peat and AAMP was placed in a 250 cm^3 flask separately. Thereafter, an aliquot of 25.0 cm^3 of 0.10 M NaOH, 0.10 M $NaHCO_3$ and 0.05 M Na_2CO_3 (for the determination of acidic groups) and 0.10 M HCl (for the determination of basic groups) was separately added to both raw and AAMP samples. The mixtures were shaken for 24 h. After filtering the mixtures, 10.0 cm^3 of each filtrate was pipetted out and the excess of base and acid was titrated with 0.10 M HCl or NaOH, respectively, using Tashiro indicator. All the experiments were performed in triplicate for more reliable results.

2.3.2.4. SEM analysis

To determine the interaction between Ni(II) with peat, microscopic adsorption sites of raw peat and modified peat ($d < 0.063$ mm) were investigated by observing SEM images.

2.3.2.5. Determination of surface area

A sample of 0.100 g of AAMP was shaken with 10.00 cm^3 of deionized water (Solution A). A sample of 0.0120 g of methylene blue dye was dissolved in 100.00 cm^3 of deionized water (Solution B). Then, Solutions A and B were allowed to mix for 2.0 h, and the mixture was allowed to stand overnight. Thereafter, 5.00 cm^3 aliquot of the supernatant solution was removed and centrifuged. The concentration of methylene blue in the supernatant solution was determined by taking absorbance measurements at 662 nm. The same procedure was followed using different concentrations of methylene blue solutions.

2.3.2.6. Point of zero charge (PZC)

For surface titrations, a sample of 0.75 g of AAMP stirred with 125 cm^3 of 0.10 mol dm^{-3} $NaNO_3$ solution was used. The resulting suspension was titrated up to the pH of 10.0 with a NaOH solution (0.10 mol dm^{-3}, standardized with the secondary standard HNO_3 acid of 0.0920 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 and 0.0010 mol dm^{-3}. Changes in pH of peat suspensions were recorded when the NaOH solution was added dropwise. Finally, the plot of surface charge density versus pH was constructed for three ionic strengths in order to determine the point of zero charge.

2.3.3. Optimization of experimental parameters for Ni(II) – peat interactions

Weighed samples of chemically modified peat ($d < 1.0$ mm) were added to 50.00 cm^3 of Ni(II) solutions placed in small jars. Each sample was shaken for a specified period of time and allowed to settle for a specified period of time. Then, the suspension was filtered, and the filtrate was analyzed for total Ni concentration using AAS. The percentage removal was calculated using Eq. (1)

$$\text{Percentage removal} = \frac{C_i - C_f}{C_i} \times 100\% \tag{1}$$

where C_i is initial concentration of Ni(II) in solution and C_f is final concentration of Ni(II) in the filtrate after treatment. The concentrations, C_i and C_f, were determined with the help of a calibration curve constructed daily. All the experiments were carried out in triplicate, and the average values were reported.

2.3.3.1. Optimization of different acid concentrations

The concentration of different acid solutions (HNO_3, HCl, CH_3COOH and $H_2C_2O_4$) were optimized for the removal of Ni(II) by shaking with a solution of Ni(II) with peat treated with each acid. For this purpose, 50.00 cm^3 aliquots of 10.00 mg L^{-1} Ni(II) solutions were mixed separately with weighed samples of peat and thoroughly stirred at a speed of 150 rpm for 1.0 h, followed by a constant settling time of 1.0 h.

2.3.3.2. Optimization of dosage

The dosage of AAMP was optimized by shaking 50.00 cm^3 aliquots of 10.00 mg L^{-1} Ni(II) solutions, with AAMP samples of mass ranging from 0.300 g to 10.000 g. Each solution was stirred at a speed of 150 rpm for 1.0 h, followed by a constant settling time of 1.0 h.

2.3.3.3. Optimization of stirring time and settling time

Aliquots of 50.00 cm^3 of 10.00 mg L^{-1} Ni(II) solutions were separately stirred at a speed of 150 rpm with AAMP of optimized dosage for different shaking times ranging from 0 min to 150 min, followed by a constant settling time of 1.0 h. After optimizing the shaking time, the same experiments were carried out to optimize the settling time using the predetermined optimum dosage and stirring time. Settling time was varied from 0 min to 60 min to determine the optimum value.

2.3.3.4. Optimization of initial solution pH for metal adsorption

Initial pH of Ni(II) solutions were varied ranging from 1.00 to 7.00, and the extent of removal was determined, at the optimum values of dosage, stirring and settling times.

2.3.4. Isotherm studies

Solutions of Ni(II) of initial concentration varying from 10 to 2000 mg L^{-1} were shaken with AAMP under optimized conditions of dosage, shaking time, settling time and pH. Each solution was then allowed to reach equilibrium, and the concentration of Ni(II) in the supernatant solution was determined. The extent of adsorption was determined as the mass of Ni(II) adsorbed (in mg) on 1.00 kg of the treated peat. The extent of adsorption was plotted against the initial Ni(II) concentration to check the validity of the Langmuir and Freundlich isotherms, whose linearized forms are given below [18].

Langmuir isotherm,

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{K_L q_{\max}} \tag{2}$$

and Freundlich isotherm,

$$\log q_e = \log K_L + \frac{1}{n}\log C_e \tag{3}$$

where q_e is the mass of Ni(II) adsorbed from solution at equilibrium (mg kg^{-1}), $q_{\max}$ is the adsorption capacity (mg kg^{-1}), K_L is Langmuir constant (L mg^{-1}), C_e is concentration of Ni(II) in solution at equilibrium (mg L^{-1}), K_f is the Freundlich adsorption constant (mg kg^{-1}) and n is a dimensionless constant. Subsequently, the isotherm constants of these models were calculated, and the adsorption capacity for Ni(II) was determined.

2.3.5. Kinetics studies

Kinetics experiments were carried out at ambient temperature (25°C). First, 1.000 g of AAMP was added to 990 cm^3 of 10.0 mg L^{-1} Ni(II) solution, and stirred slowly with a magnetic stirrer. While stirring, 5.00 cm^3 aliquots of the supernatant solutions were withdrawn at regular intervals of 1 min for a period of 30 min, and another sample was withdrawn after 60 min to determine the equilibrium state concentration. Then, the Ni concentration in each sample was determined by AAS, and the extent of adsorption was calculated. The data obtained were used to plot first order, second order and pseudo-second order kinetic models, whose linearized forms are given below [19,20]:

Pseudo-first order kinetic model,

$$\log\left(q_e - q_t\right) = -\frac{k'}{2.303}t + \log q_e \tag{4}$$

Second order kinetic model,

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

Pseudo-second order kinetic model,

$$\frac{t}{q_t} = \frac{1}{q_e}t + \frac{1}{k'q_e^2} \tag{6}$$

where k' is apparent rate constant, t is contact time; q_e and q_t are the masses of metal ion sorbed by unit mass of sorbent at equilibrium and at time t.

2.3.6. Desorption studies

After completion of adsorption experiments with AAMP, Ni(II)-adsorbed AAMP samples were allowed to air-dry, and a sample of 1.00 g was shaken with 50.0 cm^3 of pH-adjusted deionized water for 1.0 h and allowed to settle for 1.0 h. Then, the concentration of Ni(II) leached out was determined to calculate the extent of desorption. Desorption experiments were repeated for different initial pH values in the range from 1.0 to 11.0.

3. Results and discussion

3.1. Chemical modification of eat

3.1.1. Optimization of acid concentration for chemical modification of peat

The removal percentage of Ni(II) by natural MP is low, as reported earlier [17]. Further, thermal modification of peat does not give considerable enhancement of removal, indicating that organic matter and surface functionalities present in peat do not affect significantly on Ni(II) removal. Therefore, chemical modification is used to enhance the interaction between Ni(II) and peat. Fig. 1 shows the extent of removal of Ni(II) by raw peat and thermally treated peat (at 200°C) with and without treatment of HNO_3 and HCl.

According to the observations given in Fig. 1, removal percentage of Ni(II) for HNO_3 and HCl treated raw peat ranged between 70% and 90%, while that of Ni(II) for HNO_3 and HCl treatment of thermally treated peat ranged between 80% and 100%. Although thermally treated peat shows higher removal than raw peat, turbidity in the filtrate of the former was higher, probably due to the combustion reactions and various other reactions that would have occurred upon thermal modification. Therefore, raw peat was selected for further acid treatment. Other than HNO_3 and HCl, raw peat modified with CH_3COOH and $H_2C_2O_4$ solutions having

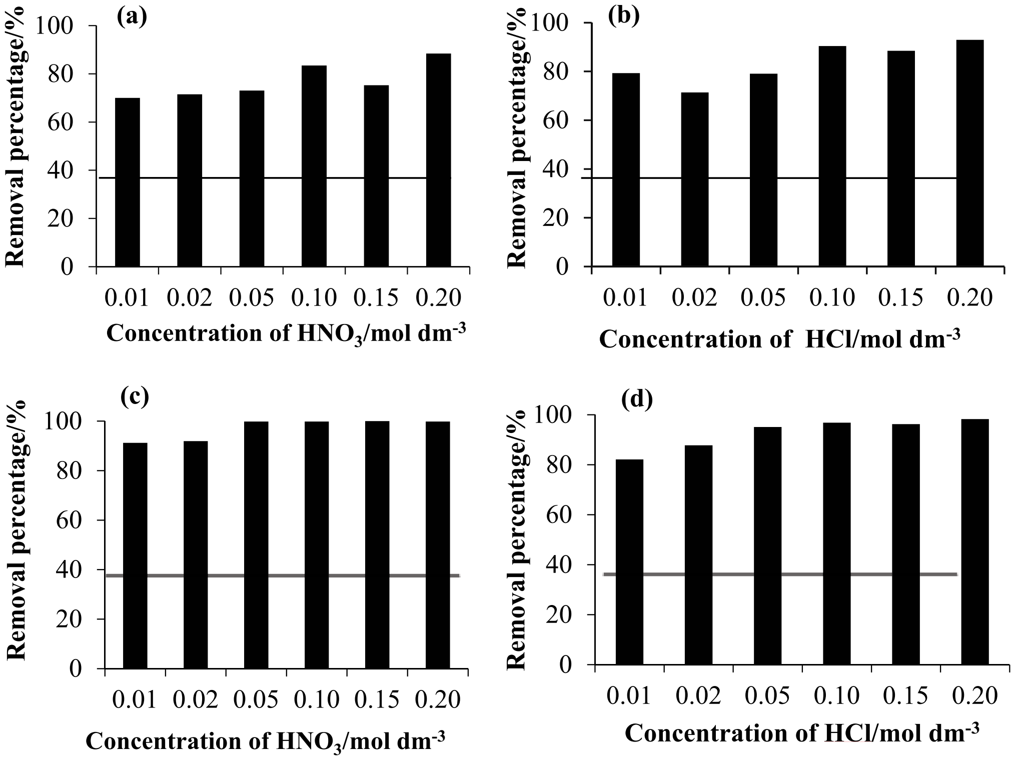

Fig. 1. Removal percentage of Ni(II) by different peat samples [5.00 g peat, 50.00 cm^3 of 10.0 mg L^{-1} Ni(II), 1.0 h stirring time, 1.0 h settling time]; (a) HNO_3 treated raw peat, (b) HCl treated raw peat, (c) Peat heated at 200°C followed by HNO_3 treatment, (d) Peat heated at 200°C followed by HCl treatment. The horizontal line shows the extent of Ni(II) removal by raw peat without any treatment.

concentrations ranging from 0.01 to 0.20 mol dm^{-3} led to the results given in Fig. 2.

According to Figs. 1 and 2, the removal percentage of Ni(II) is enhanced with acid treatment, during which organic matter would be digested resulting in activation and expansion of adsorption sites. Further, acidification results in protonation of functional groups available on the peat surface promoting ion exchange properties for easy exchange with Ni(II) [9]. These processes would enhance the Ni(II) removal ability of acid modified peat. An undesirable fact, however, is that acid modified peat leads to enhanced turbidity with the exception of AAMP. This is probably due to stronger protonation of surface functional groups and more efficient digestion of organic matter in peat by strong acids, such as HNO_3 and HCl. Further, the first ionization constant (K_{a1}) of $H_2C_2O_4$ is 5.6 × 10^{-2} mol dm^{-3}, which is much higher than that of CH_3COOH, which has a value of 1.8 × 10^{-5} mol dm^{-3}. Bidentate nature of $H_2C_2O_4$ and the higher K_{a1} value make it more reactive than CH_3COOH. Therefore, $H_2C_2O_4$ could also take part in the reactions that would take place during the treatment of strong acids to a less extent. For these reasons, turbidity of $H_2C_2O_4$ modified peat is higher than AAMP. The above argument is further supported by the observation that the turbidity is increased with the strength of the acid used. This turbidity effect not only limits accurate measurements of the final concentration of Ni(II), but also is a drawback for large scale applications in real situation. Although peat treated with strong acids, such as HCl and HNO_3, and $H_2C_2O_4$, shows little higher removal ability toward Ni(II), AAMP was selected to remove Ni(II) in subsequent studies as a compromise by considering both removal ability and turbidity, both of which are important factors in real applications.

3.2. Characterization of acetic acid modified peat (AAMP)

3.2.1. Bulk characterization

XRD patterns obtained for both raw peat and AAMP provide evidence for the presence of crystalline substances along with a significant amount of amorphous matter (Fig. 3). Quartz, pyrite, kaolin, goethite and halloysite are possible minerals present in peat in considerable quantities. However, the formation of a few new peaks in the XRD pattern for AAMP could be attributed to the decomposition of amorphous compounds, such as humic acid, exposing crystalline minerals during acid treatment. Further, the XRD pattern of AAMP shows decreasing peak intensity at the 2-theta value of 28, indicating the crystalline mineral nature of quartz. This observation is probably due to the loss of crystalline properties of minerals upon acid treatment. Nevertheless, as peat is a heterogeneous mixture of different crystalline and amorphous substances, conclusive description of peat cannot be achieved by XRD analysis alone.

Generally, adsorption capacities of adsorbents toward metal ions depend on the chemical reactivity of functional groups and porosity [21]. FTIR spectroscopic analysis is a powerful tool for identification of functional groups. According to Fig. 4, the FTIR spectrum obtained for raw

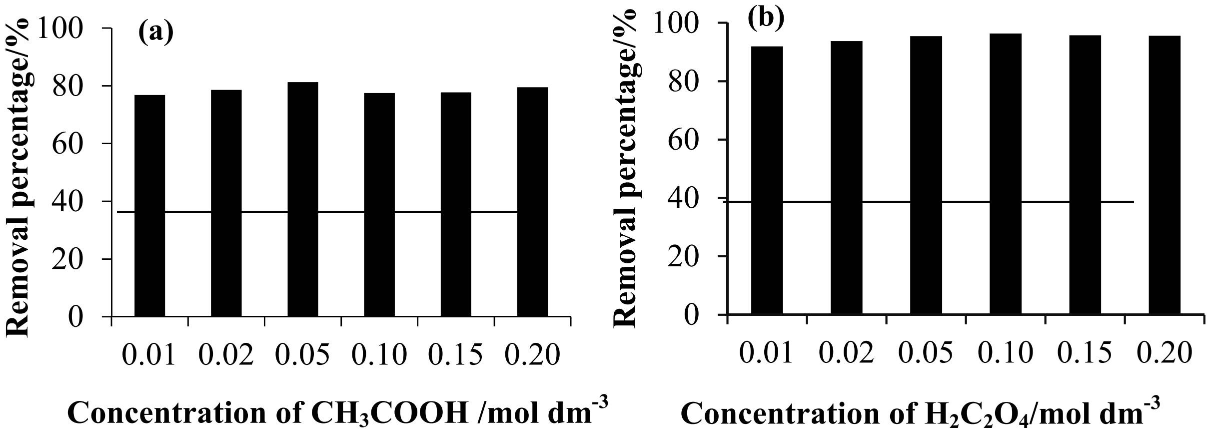

Fig. 2. Removal percentage of Ni(II) by peat; (a) CH_3COOH treated raw peat, (b) $H_2C_2O_4$ treated raw peat [5.00 g peat, 50.00 cm^3 of 10.0 mg L^{-1} Ni(II), 1.0 h stirring time, 1.0 h settling time].

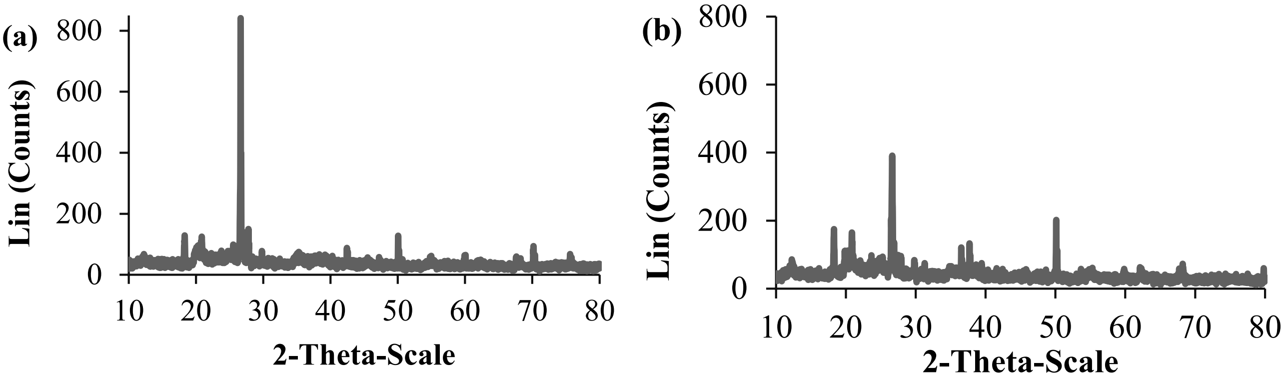

Fig. 3. XRD patterns for (a) raw peat and (b) AAMP.

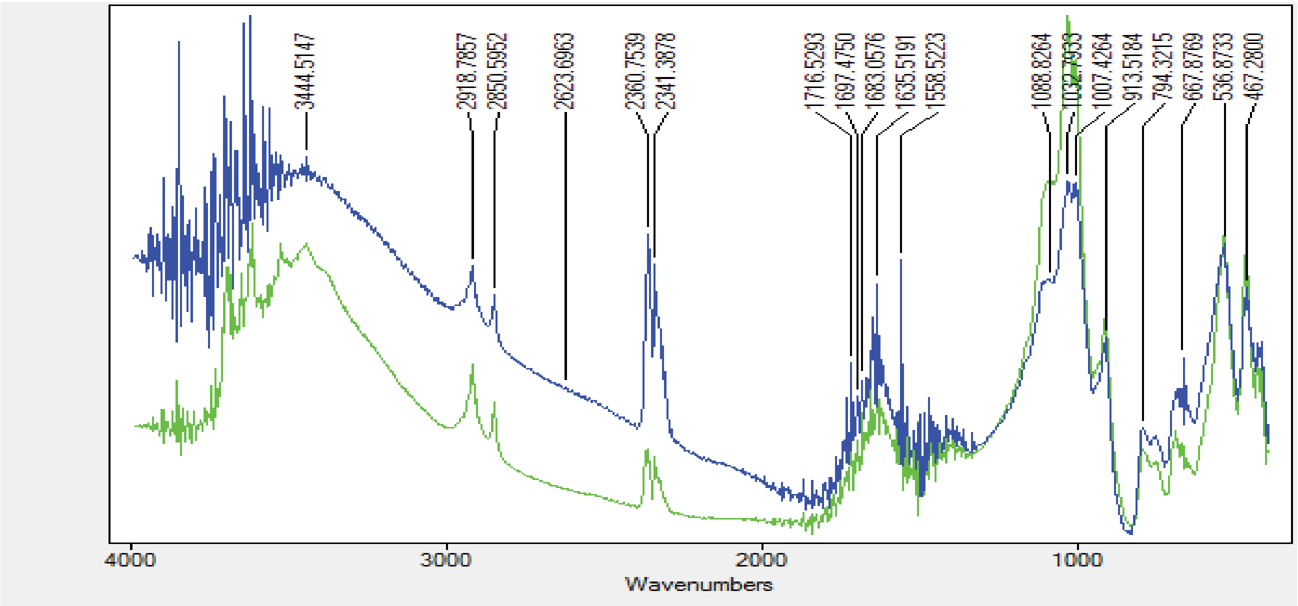

Fig. 4. FTIR spectra for raw peat (blue) and AAMP (Green).

peat is similar to that is reported in previous studies [17]. However, peak positions of FTIR spectra recorded for raw peat and AAMP are not much changed (Fig. 4). This indicates the presence of functional groups, such as alcoholic-OH or N-H stretching (peaks at 3400–3700 and 3300–3500 cm^{-1}), carboxylic groups –OH (2500–3100 cm^{-1}), ketone groups (1716 cm^{-1}), alkyne C bonds (2200–2400 cm^{-1}), aromatic C-O bonds (1641–1737 cm^{-1}), C=C stretching (1546–1652 cm^{-1}), C-C stretching (1007–1033 cm^{-1}), C=C trans bonds (912 cm^{-1}), Si-O (1080–1090 cm^{-1}) and Si-H (469–800 cm^{-1}) of silicate impurities remained unchanged during acetic acid treatment. Therefore, a conclusive description would not be feasible by FTIR spectrum alone. Further, according to XRF, both raw peat and AAMP are found to contain the same elements; K, Ca, Ti, Fe and S, which is supported by previous studies [17].

Surface oxygen functional groups were determined according to the Boehm's method. According to this method, the numbers of acidic sites present in both raw peat and AAMP were calculated under the assumption that NaOH neutralizes carboxyl, phenolic and lactonic groups; Na_2CO_3 neutralizes carboxyl and lactonic groups, and $NaHCO_3$ neutralizes only carboxyl groups. The number of surface basic sites were calculated by considering the amount of HCl required. Table 1 shows the results obtained from Boehm titration method. According to the results obtained, the total number of acidic groups and phenolic groups in AAMP was less than that in raw peat while the total number of basic groups in of AAMP was higher than that in raw peat. Further, there is no change in both lactonic groups and carboxylic acid groups while carboxyl groups of both samples were zero indicating that these groups may not be titratable under the conditions provided.

3.2.2. Surface characterization

SEM images for AAMP before and after treatment with Ni(II) are shown in Fig. 5. The SEM image of raw peat without any adsorption is also shown for comparison. According to the Figure, AAMP particles show more pores than raw peat, indicating increased surface area during acid treatment supporting the previous observations. Adsorption of Ni(II) on AAMP leads to the reduction of pore structure, confirming its adsorption on the surface of treated peat.

Surface area of an adsorbent can be determined using the adsorption of methylene blue (MB), a cationic dye, on the surface of AAMP. The point of completion of adsorption, that is, cation replacement process, where the amount of methylene blue adsorbed becomes a constant, can be used to determine the specific surface area (S_s), using Eq. (7),

Table 1
Surface oxygen functional groups by Boehm method.

Sample	Raw peat	AAMP
Basic groups, mmol g^{-1}	0.40	0.50
Total acidic groups, mmol g^{-1}	1.20	0.30
Caboxylic groups, mmol g^{-1}	0	0
Lactonic groups, mmol g^{-1}	0.05	0.05
Phenolic groups, mmol g^{-1}	1.15	0.25

$$S_s = \frac{m_{MB} A_v A_{MB}}{m_s M} \tag{7}$$

where S_s is the surface area of acetic acid treated peat (m^2 g^{-1}), m_{MB} is the mass of MB adsorbed at the point of complete cation replacement (g), A_v is the Avogadro constant, A_{MB} is the area covered by a MB molecule (1.30 × 10^{-20} m^2), m_s is the mass of AAMP sample, and M is the molar mass of MB (319.87 g mol^{-1}). Surface area of AAMP determined at the saturation point of MB adsorbed, as noticed in Fig. 6, with the aid of Eq. (7) is 8.6 m^2 g^{-1}. This value is greater than that of raw peat (4.9 m^2 g^{-1}), reported in previous studies [17]. The increase in the surface area is about 76%, which demonstrates the superior nature of AAMP for adsorption of metal ions.

The point of zero charge (PZC) is an important characteristic of amphoteric colloids and suspensions. Surface charge in these systems depends on activities of potential-determining ions (H^+ and OH^-) and electrolyte concentrations (ionic strength). Depending on the surrounding pH, adsorbent surface can be negative, positive or having no charge. The pH at which the net total particle charge is zero is called the PZC. If the surrounding pH is above its PZC, the adsorbent surface bears a net negative charge, showing its ability to exchange cations, and vice versa [22]. The PZC for AAMP determined using surface charge density - medium pH curves constructed in $NaNO_3$ solutions of different ionic strengths. Charge densities at different pH values were calculated using Eq. (8) [23],

$$\sigma = \frac{F}{a \times s}\left\{\left(C_a - C_b\right) - [\mathrm{H}^+] + [\mathrm{OH}^-]\right\} \tag{8}$$

where σ is the charge density of the surface, F is the Faraday constant, a is the specific surface area, s is the composition of AAMP particles in the suspension, [H$^+$] and [OH$^-$] are the equilibrium concentrations of hydronium and hydroxyl ions, C_a is the initial acid concentration, and C_b is the initial base concentration. The PZC of AAMP is 4.5, based on the point of intersection of the curves obtained in $NaNO_3$ solutions of 0.01 and 0.001 mol dm^{-3}. The curve obtained for 0.1 mol dm^{-3} is very close to the first two, and it is parallel to that in 0.001 mol dm^{-3} $NaNO_3$, indicating that the pH independent surface charge of AAMP particles is more predominant, as compared with the pH dependent charge.

According to Table 2, the PZC of AAMP is higher than that of raw peat, which could be due to the loss of organic matter, in particular, compounds containing phenolic and carboxylic groups during acid treatment. Therefore, higher medium pH would be required to maintain the surface neutrality of AAMP.

3.3. Optimization of parameters for removal of Ni(II) by AAMP

The extent of removal of an adsorbent, usually expressed as the percentage removal, depends on several experimental parameters, including dosage of adsorbent, stirring time, settling time, initial solution pH and pre-treatment conditions. Therefore, the optimum values of the above experimental parameters should be determined for the most efficient removal. In this regard, effect of one parameter on the percentage removal should be studied by changing the

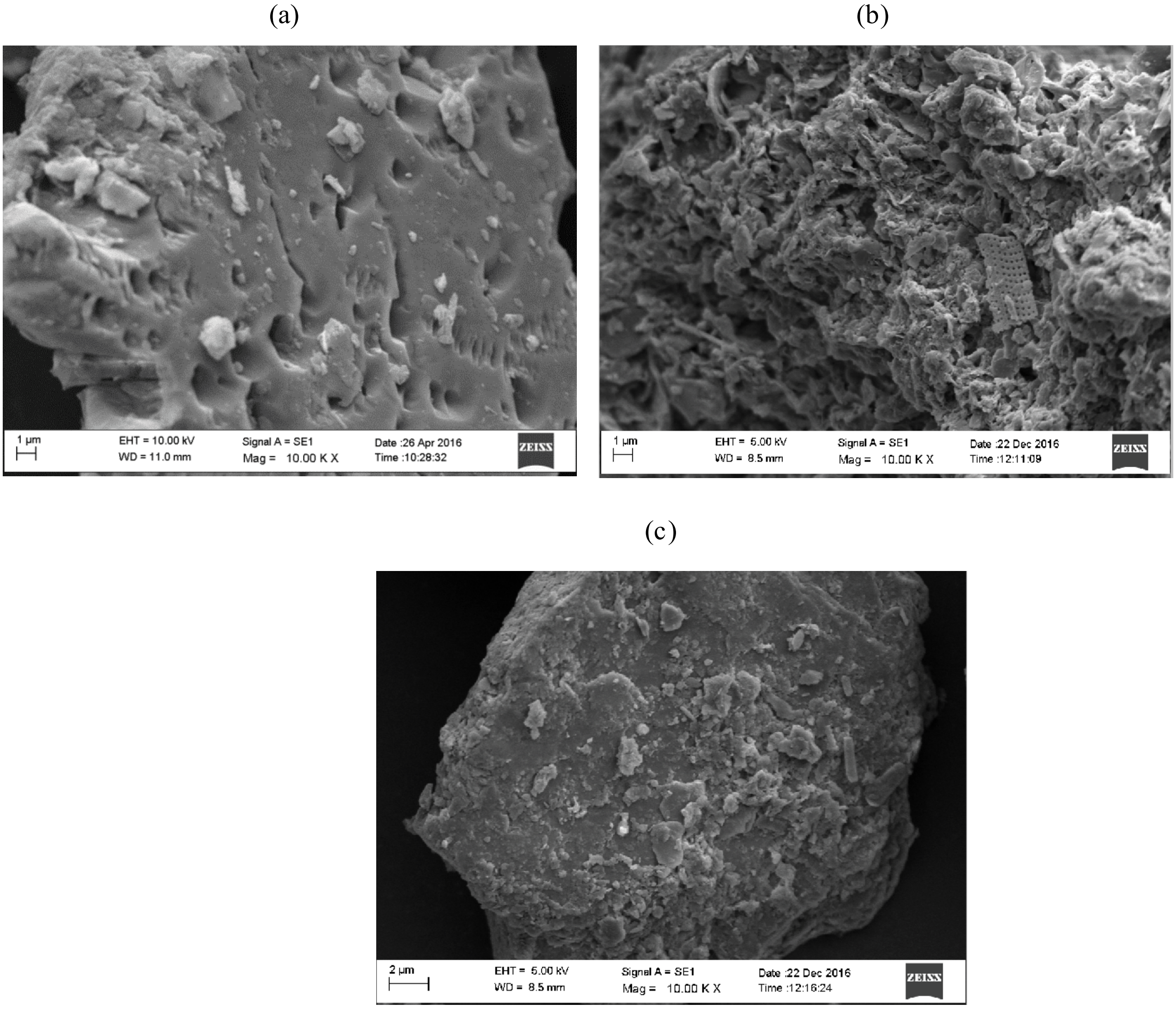

Fig. 5. SEM images for (a) raw peat, (b) AAMP, (c) after adsorption of Ni(II) on AAMP.

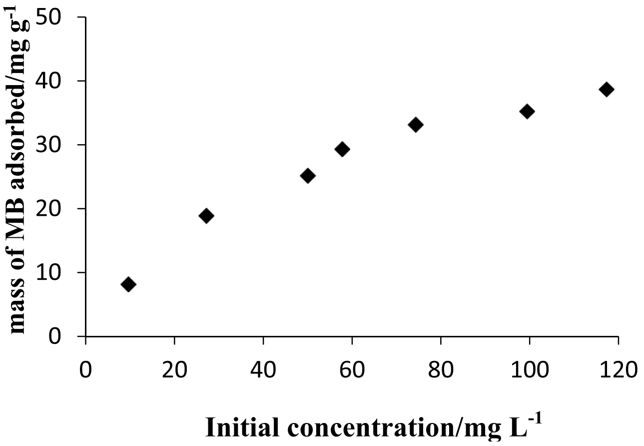

Fig. 6. Variation of mass of MB adsorbed with the initial concentration (0.100 g AAMP, 2.0 h stirring, 12.0 h settling time).

Table 2
PZC of raw peat and modified MP particles.

Adsorbent	PZC	Reference
Raw peat	3.8	[17]
Peat treated at 200°C	4.2	[17]
Peat treated at 400°C	8.5	[17]
Extracted HA from MP	3.7	[24]
AAMP	4.5	This study

parameter selected, while keeping the other parameters constant.

3.3.1. Optimization of concentration of acetic acid

The extent of removal of Ni(II) from a 10.0 mg L^{-1} solution by peat modified with CH_3COOH solutions of different concentrations ranging from 0.01 to 0.20 mol dm^{-3} is determined to be concentration independent. Therefore, 0.01 mol dm^{-3}, the lowest concentration attempted, is recommended as the optimum concentration to modify peat for Ni(II) removal studies.

3.3.2. Optimization of dosage

The extent of removal of Ni(II) by AAMP for different dosages indicates in Fig. 7. The optimum dosage selected for the removal of Ni(II) was 5.00 g, beyond which it showed almost constant extent of removal.

3.3.3. Optimization of stirring time

The removal percentage of Ni(II) was increased significantly during the initial 30 min period and thereafter it remains almost constant. Therefore, the optimum stirring time for removal of Ni(II) was selected as 45 min (Fig. 8).

3.3.4. Optimization of settling time

It was experimentally determined that the removal percentage remained almost the same during the entire settling time period. Similar results have been reported in many adsorbate-adsorbent systems when natural substances are used as adsorbents to remove heavy metal ions [17]. However, a small settling time period of 20 min was taken as the optimum for the removal of Ni(II) ions.

3.3.5. Optimization of medium pH

Medium pH is an important parameter which affects the removal of heavy metals as the solubility of metal ions depends on the medium pH. The removal percentage with pH was investigated from varying values of pH from 1.0 up to a value at which corresponding hydroxide precipitation occurs. When pH is increased, the removal percentage in each metal ion increases as shown in Fig. 9.

At lower pH values, H$^+$ ions predominantly cover adsorption sites on the surface of the adsorbent. Therefore, it is not allowed to interact with metal ions, resulting in lower extent of removal at lower pH values [9]. The removal percentage increases with the increase in pH, and becomes constant after a certain pH. Accordingly, the optimum pH range for Ni(II) was selected as 5.0–6.0. Therefore, all the experiments were carried out by adjusting the initial pH within this range.

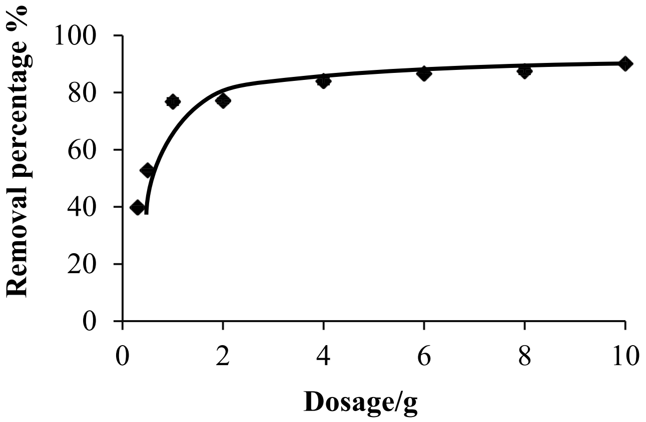

Fig. 7. Removal percentage of Ni(II) by AAMP at different dosages [1.0 h shaking time, 1.0 h settling time 50.00 cm^3, 10.0 mg L^{-1} Ni(II) solution].

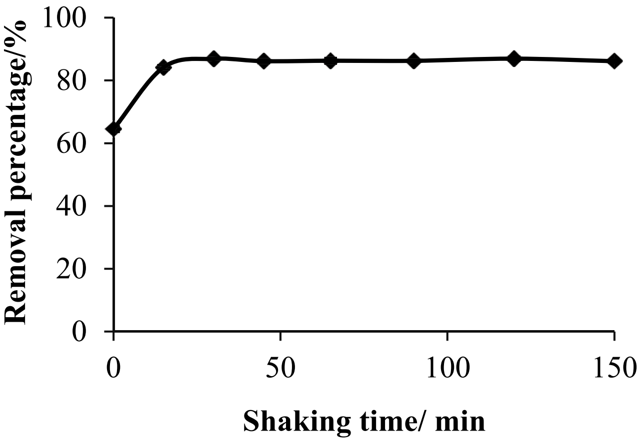

Fig. 8. Removal percentage of metal ions by AAMP for different shaking times [1.0 h settling time, 50.00 cm^3 10.0 mg L^{-1} Ni(II) solution].

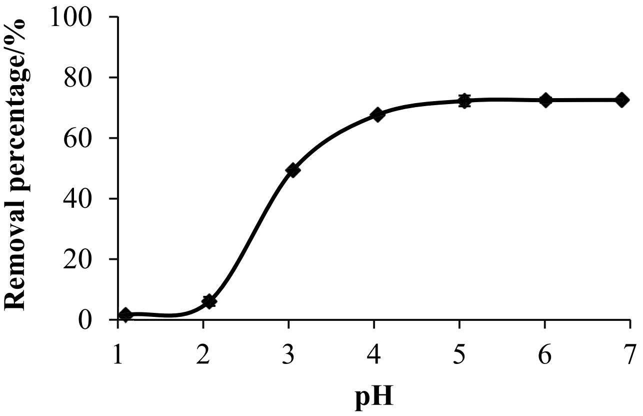

Fig. 9. Removal percentage of metal ions by AAMP for different pH values, for 50.00 cm^{3}of 10.0 mg L^{-1} Ni(II) solution under optimized shaking and settling times.

3.4. Isotherm studies on AAMP

According to Fig. 10, the variation of the amount of Ni(II) adsorbed on AAMP with respect to the initial concentration reflects Type IV isotherm [25]. This suggests mesoporous characteristics of the adsorbent, and describes the formation of a monolayer followed by a multilayer. The monolayer formation is completed at an initial concentration of 400 mg L^{-1} of Ni(II), and the overall adsorption completes at 1200 mg L^{-1} concentration.

Langmuir and Freundlich adsorption isotherms are the most widely used isotherm models, which are used to study the adsorption behavior of metal ion-adsorbent systems. The linear form of the Langmuir adsorption isotherm plotted according to Eq. (2) is shown in Fig. 11, while the linear form

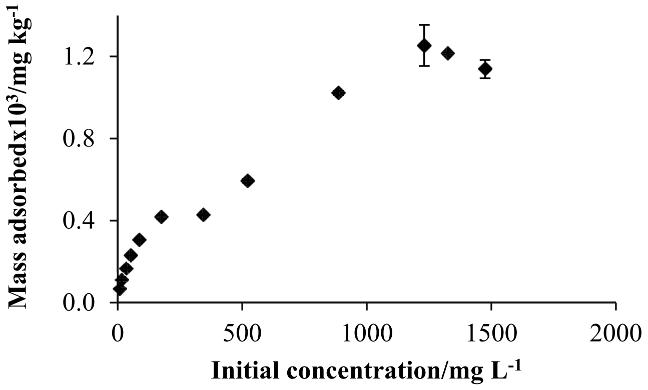

Fig. 10. Amount of Ni(II) adsorbed on AAMP, under optimized conditions, for different initial concentrations of 50.00 cm^3 Ni(II) solution.

of the Freundlich isotherm plotted according to Eq. (3) is shown in Fig. 12.

The linear regression coefficient of the Langmuir fit for the entire range of concentrations and the low concentration range, and that of the Fruendlich fit for the entire range of concentration, are 0.878, 0.960 and 0.979, respectively. According to the regression coefficient values, the Langmuir isotherm fits at only low concentrations and the Freundlich isotherm fits within the whole range of concentrations investigated. Therefore, by considering both the regression coefficient and the agreement with the conditions of Type IV isotherm, it is reasonable to assume that the Ni(II)–AAMP system is best described by the Fruendlich adsorption isotherm, which leads to n and K_F values of 0.441 and 4.80×10^1 L mg^{-1}, respectively. The n value being less than 1.0 indicates normal adsorption [26]. Further, the maximum mass of Ni(II) per unit mass of adsorbent (q_{max}), determined from the Langmuir plot within the low concentration range is 6.24×10^2 mg kg^{-1}. It is thus clear that peat after treatment with acetic acid (AAMP) is an effective adsorbent to remove Ni(II). Although peat has been investigated as a strong biosorbent for Ni(II) and other metal ions from aqueous solution [27–30], enhancement of biosorption characteristics of peat toward Ni(II) through chemical modification has not been paid much attention, probably due to the complex nature of such systems. Further, as the composition of peat with regard to humic acid varies depending on geographic and climatic conditions, adsorption capacity of peat or modified peat would vary with the location.

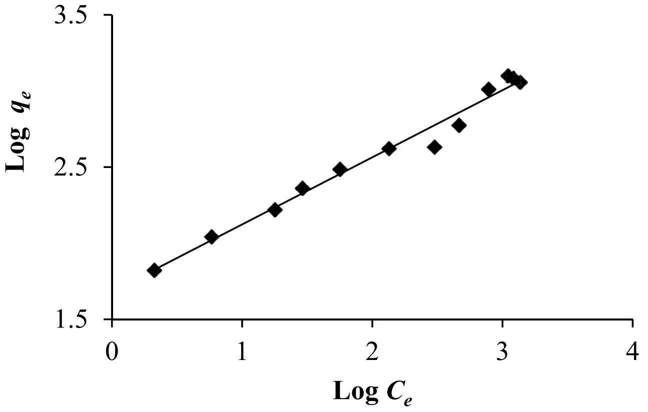

Fig. 12. Freundlich adsorption isotherm model for Ni(II)–AAMP interaction under optimized conditions.

3.5. Kinetics modeling

The two reactants of the Ni(II)–AAMP heterogeneous system are Ni(II) concentration in the solution phase and the number of adsorption sites of AAMP. As it is difficult to change the latter, kinetics studies of Ni(II) adsorption of AAMP could be investigated by monitoring the concentration of Ni(II) in solution phase as a function of contact time keeping the mass of AAMP (i.e., the number of adsorption sites) constant, which leads to pseudo order kinetics. The pseudo order models describe how the rate depends on the equilibrium sorption capacity [27].

According to regression coefficients, the application of adsorption kinetics data obtained every 1 min immediately after the progress of the sorption reaction of Ni(II) for the linearized pseudo first order model [Eq. (4)] and the second order model [Eq. (5)] does not lead to satisfactory agreement;

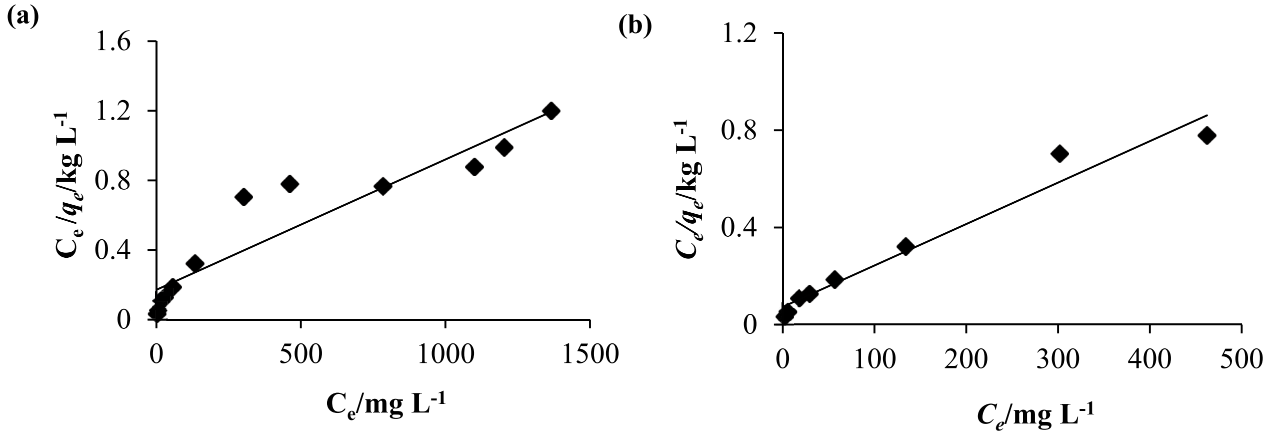

Fig. 11. Langmuir adsorption isotherm model for Ni(II)–AAMP interaction under optimized conditions: (a) wider concentration range and (b) low concentration range (<500 mg L^{-1}).

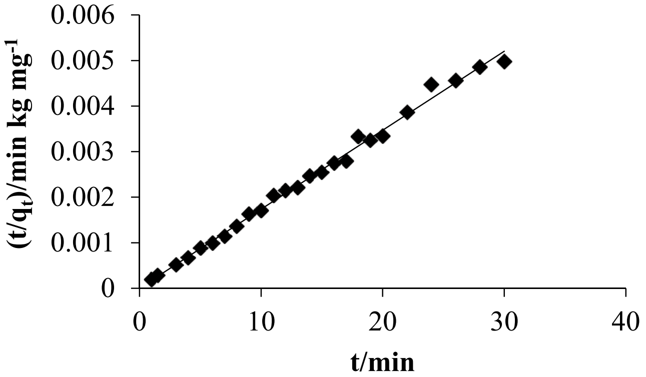

Fig. 13. Pseudo-second order kinetics model for the interaction of Ni(II)–AAMP with 10.0 mg L^{-1} solution.

but is in good agreement with the pseudo second order model [Eq. (6)] with a regression coefficient of 0.994 (Fig. 13), indicating that chemisorption of Ni(II) is the main mode of mass transfer for adsorption, which would occur through bond formation with electronegative moieties present on the surface of peat, such as carboxylic and phenolic acid groups. Further, the pseudo second order rate constant determined from the plot of Fig. 13 is 6.03 × 10^{-3} kg mg^{-1} min^{-1}, which is a measure of the adsorption rate. Sorption of many metal ions on natural sorbents, such as food waste, clay types, rice husk, maize bran and tree fern have been reported to obey pseudo second order kinetics supporting the above finding [9].

3.6. Desorption studies

Desorption experiments carried out by changing the initial solution pH of the eluent indicates that the extent of desorption increases with increasing the acidity of the medium, and the amount of adsorbed Ni(II) that is leached out to the solution is not significant at pH > 5.0. It is thus confirmed that Ni(II) adsorbed AAMP would not contaminate water under normal conditions, such as rain events.

4. Conclusion

The low extent of removal of Ni(II) by natural peat available in Muthurajawela, Sri Lanka, is not enhanced with thermal treatment. Chemical treatment, which affects chemical and physical properties, such as topology and three dimensional structure of the matrix, conducted with hydrochloric acid, nitric acid, oxalic acid and acetic acid, enhances the affinity of peat toward Ni(II). By considering both the extent of removal and the turbidity of the resulting solution, both of which are important aspects in large-scale treatment of industrial effluents, acetic acid was selected to be the most efficient modifier of peat for adsorption of Ni(II), probably due to protonation of surface functional groups of peat without much damage to the surface characteristics. The optimum values determined by varying one parameter at a time, keeping others unchanged, are 0.01 mol dm^{-3} acetic acid concentration, 5.000 g dosage (mass of peat), 45 min shaking time, 20 min settling time and 5.0–6.0 pH. The sorption process of Ni(II) on acetic acid modified peat (AAMP) obeys the Freundlich adsorption isotherm, and the Langmuir adsorption isotherm at low concentrations, indicating that Ni(II) corresponds to multilayer formation after completion of the monolayer. The adsorption capacity of Ni(II) on AAMP is 6.24 × 10^2 mg kg^{-1}, an enhancement as compared with that of natural peat. The interaction between Ni(II) and AAMP follows pseudo second order kinetics with a rate constant of 6.03 × 10^{-3} kg mg^{-1} min^{-1}, indicating that chemisorption has involved in the adsorption process.

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