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Adsorption of Divalent Metal Ions on a Herbaceous Peat

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This study was performed to determine divalent metal ion [Cu(II), Zn(II), Mn(II) and Ni(II)] adsorption characteristics of the herbaceous peat of the Gavur Lake, Turkey. The adsorption data of the metal ions were fitted to both the Langmuir and the Freundlich isotherms. The adsorption capacity of the peat was much higher for Cu (38.5 mg g^{-1}) compared with Zn (28.0 mg g^{-1}), Mn (26.4 mg g^{-1}) and Ni (24.1 mg g^{-1}). A steady increase in equilibrium Ca and Mg ion concentrations were measured as initial metal ion concentrations increased from 1×10^{-3} M to 5×10^{-3} M in Cu and Zn adsorption experiments indicating that ion exchange was an important mechanism in the adsorption. The kinetic study revealed that the adsorption followed the pseudo-second-order model and the interaction between the metal ions and the peat was very fast, especially for Cu. The pH study revealed that Cu adsorption was not affected in the pH range between 3 and 5, but the adsorption of Zn, Mn and Ni was lower at pH 3 compared with pH 4 and 5.

Key Words: Adsorption, Kinetics, Peat, Copper, Zinc, Manganese, Nickel.

INTRODUCTION

There is an increasing environmental concern of heavy metal loading to water resources from industrial wastewater discharges. High levels of the heavy metals such as copper, zinc, manganese and nickel are harmful for many life forms and cause brain, kidney, lungs, liver and central nervous systems failure in humans[1]. Copper is released to environment *via* mining, metallurgical, fibre production, pipe production and metal plating industries. Zinc is mainly used in galvanization processes; nickel is important for electroplating and manganese finds its use in dry cell batteries, glass, ceramics, paint, varnish, ink, dyes, match and fire works[2].

Many processes exist for the treatment of wastewaters including ion exchange, precipitation, phyto-extraction, ultra-filtration, reverse osmosis and electro-dialysis and among these methods ion exchange seems most promising due to easy handling if effective and low cost sorbents are used[3]. The adsorption of metal ions from aqueous solutions has been studied using more than 70 different sorbents[4] such as perlite[5], vermiculite[6], kaolinite[7], tree fern[8], palm kernel fibre[9], carbon aerogel[2], Nipah palm shoot biomass[10], clinoptilolite[3], fly ash[11] and peat[12,13]. Peat has polar functional groups such as aldehydes, ketones and acids[13]. Metal ion adsorption by peat may take place *via* several meachanisms such as ion-exchange, surface sorption, chemisorption, complexation and sorption-complexation and it is believed that ion-exchange is the most prevalent mechanism[12]. The metal adsorption capacity of peat depends on many factors such as pH, temperature, contact time, peat doze, botanical origin of peat, metal ion and initial metal ion concentration[13,14]. This study was performed to determine Cu(II), Zn(II), Mn(II) and Ni(II) sorption characteristics of the herbaceous peat of the Gavur lake, Turkey.

EXPERIMENTAL

The herbaceous peat used in this study was obtained from the Gavur lake Peatland of Turkey. The peatland, which is surrounded by Miocene aged limestone and Paleozoic schist and serpentines formed on Holocene aged lake deposits in a closed watershed[15] on the Antakya-Kahramanmaras Graben, *ca.* 475-481 m asl, 30 km south of the Kahramanmaras city, Turkey. The area was drained by the State Hydraulic Works in the late 1950s using artificial canal networks which flow into the Aksu and Ceyhan rivers.

The peat sample was oven dried at 105 ºC and grounded through a 100 µm sieve. The soil sample was analyzed for organic matter by wet oxidation[16], pH[17] and $CaCO_3$[18]. The studied peat material has 53.6 % organic matter, neutral pH and 4.3 % total carbonate content (Table-1).

TABLE-1
SOME PHYSICAL CHARACTERISTICS OF THE PEAT MATERIAL

Organic matter (%)	53.6
pH	6.97
Total carbonate (%)	4.30

Adsorption experiment: Copper, Zn, Mn and Ni stock solutions were prepared using analytical grade $CuSO_4.5H_2O$, $ZnCl_2$, $MnCl_2.4H_2O$ and $NiCl_2.6H_2O$. A 0.5 g soil sample was weighed into a 125 mL Erlenmeyer flask and 50 mL solution containing between 1×10^{-3} M and 5×10^{-3} M concentrations of the studied metal ions (63.5-317.5 µg mL^{-1} for Cu) were added into each flask. The adsorption experiments were run in triplicates. Initial pH of the solutions was adjusted to 5, except the pH study, using 1×10^{-3} M solutions of either H_2SO_4 or NaOH. The flasks were shaken for 3 h at 21 ± 1 ºC and filtered. Equilibrium metal ion concentrations were determined using an atomic absorption spectrometer (Perkin-Elmer 3110). The amount of metal ion adsorbed by peat was calculated by the difference between the initial and equilibrium concentrations of the solutions.

In order to show the effect of cation exchange in the adsorption process, the displacement of Ca and Mg ions in Cu and Zn experiments was measured using an atomic absorption spectrometer (Perkin-Elmer 3110).

The effect of solution pH on metal ion adsorption was studied in the pH range between 3 and 5. Initial pH of the solutions was adjusted to 3, 4 and 5 using 1×10^{-3} M solutions of either H_2SO_4 or NaOH and the flasks were shaken for 3 h at 21 ± 1 ºC and filtered. The concentrations of the metal ions in equilibrium solutions were determined as mentioned above.

Kinetics of the adsorption were studied by shaking a 0.5 g peat sample with 50 mL solutions of 2×10^{-3} M and 4×10^{-3} M metal ions in a 125 mL Erlenmeyer flask. Samples were withdrawn at suitable time intervals up to 3 h, filtered and analyzed for the studied metals with an atomic absorption spectrometer (Perkin-Elmer 3110).

Theoretical: The metal adsorption by the peat was modeled using the Langmuir and Freundlich isotherms. The Langmuir model implies that the monolayer adsorption of metal ions on sorbent surface occurs, energy of sorption for each ion is same and not dependent on surface coverage and adsorption takes place only on localized sites[13]. The Freundlich model, however, assumes that the energy of adsorption decreases logarithmically as surface coverage increases due to surface heterogeneity.

Langmuir isotherm:

$$C_e/q_e = 1/kq_{max} + C_e/q_{max}$$

where q_e is the amount of adsorbed metal ion by the peat (mg g^{-1}), C_e is the equilibrium solution concentrations (mg L^{-1}), q_{max} is the adsorption maximum or the adsorption capacity (mg g^{-1}) and k is a constant related to the sorption energy (L mg^{-1}). If adsorption conforms to the Langmuir equation, a plot of C_e/q_e *vs.* C_e will form a straight line with a slope $1/q_{max}$ and intercept $1/k \times q_{max}$.

Freundlich isotherm:

$$\log q_e = \log K_f + 1/n \log C_e$$

where K_f and 1/n are constants of adsorption capacity and adsorption intensity, respectively. When Freundlich equation applies, $\log q_e$ *versus* $\log C_e$ will yield a straight line with a slope 1/n and intercept K_f.

Kinetics of the adsorption experiment was modeled using the pseudo-second order kinetics[19]:

$$t/q_t = 1/k_2q_e^2 + (1/q_e)\ t$$

and initial sorption rate calculated with the following formula:

$$h = k_2q_e^2$$

where h is the initial adsorption rate (mg g^{-1} min^{-1}), k_2 is the rate constant (g mg^{-1} min^{-1}), q_t is the amount of the metal ions on the surface of the adsorbent at any time (mg g^{-1}) and t is time (min). If the pseudo-second-order model fits the data, t/q_t *versus* t will have a straight line with a slope $1/q_e$ and intercept 1/h.

RESULTS AND DISCUSSION

Sorption isotherms: The herbaceous peat adsorbed 96 % of the Cu, Zn and Ni ions and 86 % of Mn ions at 1×10^{-3} M initial solution concentrations and the removal efficiency was similar for Cu (97 %) and lower for Zn (77 %), Mn (68 %) and Ni (75 %) at the highest initial solution concentrations (5×10^{-3} M). Figs. 1-4 show the plots of the equilibrium solution concentrations *versus* the metal ions sorbed. The adsorption data of the metal ions were fitted to both the Langmuir and Freundlich isotherms (Table-2). Figs. 5 and 6 show Langmuir and Freundlich isotherms for Cu^{2+} sorption on to the peat. Langmuir equation better explained the adsorption of the metal ions on the peat compared with the Freundlich equation based on the coefficient of determination (R^2) values (Table-2). Several studies have shown that peat-metal ion adsorption is most effectively modeled with the Langmuir isotherm[12,13]. The adsorption capacity (complete monolayer adsorption) of peat was much higher for Cu (38.5 mg g^{-1}) compared with the other metals (24.1-28.0 mg g^{-1}). The adsorption maximum of Zn, Mn and Ni was similar and the affinity of the peat for these metals decreased in the order of Zn, Mn and Ni, respectively (Table-2). Similar order of metal adsorption by peat reported elsewhere[12]. The metal adsorption capacity of peat depends on many factors such as pH, temperature, contact time, peat dose, botanical origin of peat, metal ion and initial metal ion concentration[13,14]. Ho and McKay[20] reported that the copper adsorption capacity of the eutrophic sphagnum moss peats is in the range of 10-30 mg g^{-1} and that of the oligotrophic peats is generally between 1 and 15 mg g^{-1} based on their literature review. Copper adsorption capacity of peat materials in the similar range was reported elsewhere[14,20-22].

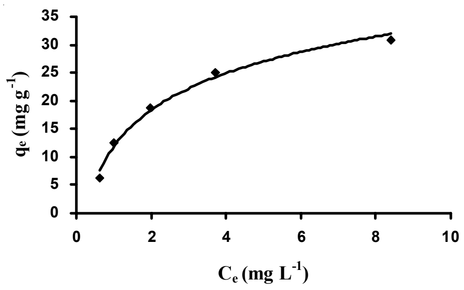

Fig. 1. Sorption isotherm of Cu^{2+}

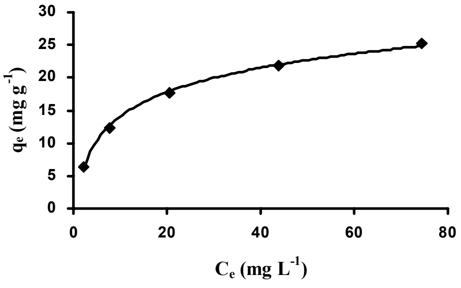

Fig. 2. Sorption isotherm of Zn^{2+}

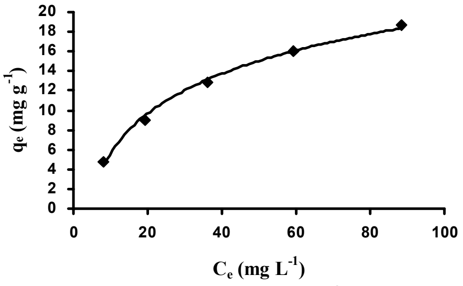

Fig. 3. Sorption isotherm of Mn^{2+}

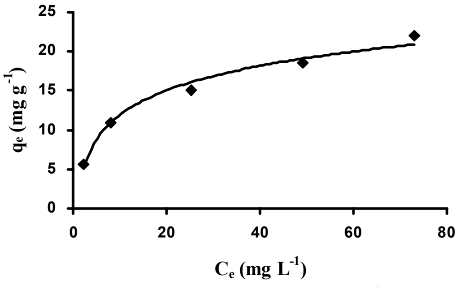

Fig. 4. Sorption isotherm of Ni^{2+}

TABLE-2
LANGMUIR AND FREUNDLICH ISOTHERM CONSTANTS
FOR THE METALS SORBED ON THE PEAT

Element	Langmuir			Freundlich		
	q_{max}	k	R^2	K_f	1/n	R^2
Cu	38.5	0.49	0.999	13.4	0.42	0.948
Zn	28.0	0.10	0.992	5.1	0.39	0.972
Mn	26.4	0.03	0.999	1.5	0.57	0.977
Ni	24.1	0.09	0.977	4.4	0.38	0.978

*q_{max} (mg g^{-1}), k (L mg^{-1}), K_f and 1/n are constants.

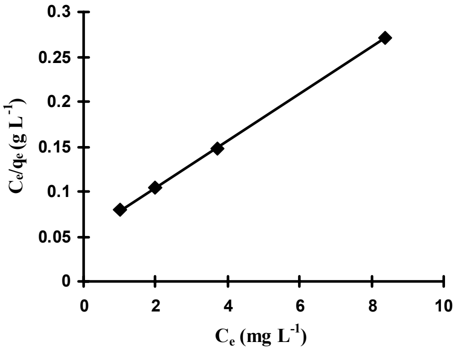

Fig. 5. Langmuir sorption isotherm of Cu^{2+} ions

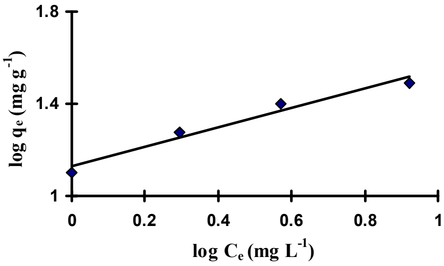

Fig. 6. Freundlich sorption isotherm of Cu^{2+} ions

The herbaceous peat material of this study has a neutral pH (6.97) and Ca and Mg are the two important exchangeable cations at this pH[15]. One of the reasons for the relatively high metal adsorption capacity of the Gavur Lake peat can be its high Ca and Mg contents on the exchange sites. Since significant correlation was found between the total exchangeable Ca and Mg contents of peats and their heavy metal adsorption capacity[12]. It was also reported[23] that heavy metals can easily displace Ca^{2+} compared to H^+. Displacement of Ca and Mg ions with metal ion adsorption was also studied in Cu and Zn experiments (Table-3). A steady increase in equilibrium Ca and Mg ion concentrations were measured as initial metal ion concentrations increased from 1×10^{-3} M to 5×10^{-3} M (Table-3). This finding, therefore, shows that ion exchange is an important mechanism in both Cu and Zn adsorption. The total displaced concentrations of Ca and Mg ions were very similar in both Cu and Zn experiments suggesting that ion exchange was not the only mechanism for the adsorption of Cu, since the peat has much higher adsorption capacity for Cu (38.5 mg g^{-1}) compared to Zn (28.0 mg g^{-1}). Chen *et al.*[24] found that the amount of released cations was less than the sorbed Cu ions. They explained this finding with the existence of another mechanism for Cu adsorption in addition to ion-exchange. Metal ion adsorption by peat may take place *via* several mechanisms such as ion-exchange, surface adsorption, chemisorption, complexation and sorption-complexation

TABLE-3
DISPLACEMENT OF Ca AND Mg IONS WITH INCREASING CONCENTRATIONS OF METAL IONS

C_i (Cu or Zn)	Cu Experiment		Zn Experiment	
	Ca	Mg	Ca	Mg
	mg g^{-1}			
1×10^{-3} M	4.1	3.9	4.1	4.1
2×10^{-3} M	6.1	4.7	5.6	4.5
3×10^{-3} M	7.6	5.2	7.0	4.9
4×10^{-3} M	9.1	5.4	9.4	5.4
5×10^{-3} M	10.3	5.6	10.9	5.4

and it is believed that ion-exchange is the most prevalent mechanism[12]. Bloom and McBride[25] reported that peat binds most divalent cations as outer-sphere complexes or by electrostatic forces with the exception of Cu, which is bound as inner-sphere complexes. The electronic properties of Cu result in formation of strong inner-sphere metal surface complexes and a very strong affinity for soil organic matter[26].

Freundlich K_f values, which is a measure of adsorption capacity ranged in the decreasing order of Cu >> Zn > Ni > Mn. The adsorption intensity values determine whether the adsorption is favourable over the entire concentration range (1/n « 1) or favourable at high concentrations and not on low concentrations (1/n > 1)[27]. The adsorption intensity constants were 0.42, 0.39, 0.57 and 0.38 for Cu, Zn, Mn and Ni, respectively, indicating activated adsorption of the metals on the peat. Chen *et al.*[28] reported that the adsorption intensity (1/n) is related to K_f in the Freundlich equation as part of the power factor and variations in intensity constant will yield exponential change in K_f. Therefore, higher 1/n value of Mn compared with that of the other metals explains why Freundlich K_f values of the metals did not rank similar to the Langmuir q_{max} values of the metals (Table-2).

Kinetic study: Kinetics of the adsorption experiments were modeled using the pseudo-second-order model[19]. The reaction between the metal ions and the peat was very fast and the system reached equilibrium within 0.5 h. The parameters of the pseudo-second-order model was calculated by regressing t/q_t *versus* t for the initial metal concentrations of 2×10^{-3} M and 4×10^{-3} M (Table-4). The kinetic data

TABLE-4
PSEUDO-SECOND-ORDER MODEL PARAMETERS OF THE METALS AT 2×10^{-3} M AND 4×10^{-3} M INITIAL SOLUTION CONCENTRATIONS

Element	2×10^{-3} M				4×10^{-3} M			
	q_e^*	h	k_2	R^2	q_e	h	k_2	R^2
Cu	12.6	169.4	1.07	0.999	24.9	145.6	0.23	0.999
Zn	12.2	54.6	0.37	0.999	21.9	149.3	0.31	0.999
Mn	9.2	60.1	0.71	0.999	16.9	47.2	0.17	0.999
Ni	10.8	51.9	0.44	0.999	19.3	79.2	0.21	0.999

*q_e (mg g^{-1}), h (mg g^{-1} min^{-1}), k_2 (g mg^{-1} min^{-1}).

showed a good fit to the pseudo-second-order model (Fig. 7). Equilibrium metal adsorption (q_e) of the peat at 2×10^{-3} M and 4×10^{-3} M initial solution concentrations were in the following order Cu > Zn > Ni > Mn. The affinity of the metals for the peat at these concentrations was similar to the rank of the Freundlich K_f values. Initial adsorption rate (h) of Cu ions (169.4 mg g^{-1} min^{-1}) was much higher than that of the other metals at 2×10^{-3} M initial solution concentrations. The adsorption rate constant (k_2) also followed the same trend. The initial adsorption rates of Cu and Mn decreased and that of Zn and Ni increased as initial metal ion concentration increased from 2×10^{-3} M to 4×10^{-3} M (Table-4). The adsorption rate constants of the studied metals, however, decreased with an increase in initial metal ion concentrations. Negative relationship between the rate constant and initial metal ion concentration was also reported elsewhere[29].

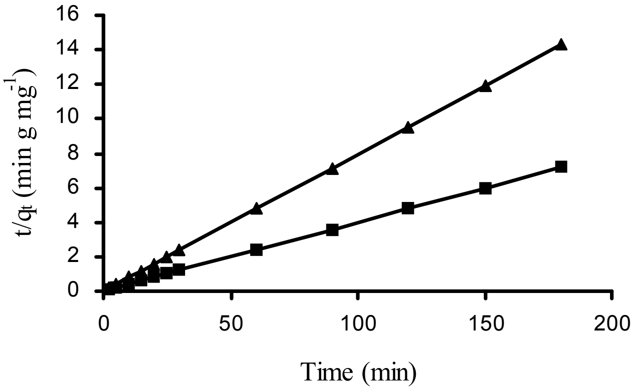

Fig. 7. Pseudo second-order kinetics of Cu^{2+} at 2×10^{-3} M (▲) and 4×10^{-3} M (■) initial solution concentrations

Effect of solution pH: Solution pH is an important factor affecting the capacity of peat to hold cations and optimum pH for adsorption[12] is between 3.5 and 6.5. The effect of solution pH on the metal adsorption was studied for solution pH values 3, 4 and 5 at 2×10^{-3} M metal ion concentrations. The equilibrium time was 3 h at 21 ± 1 ºC. Fig. 8 shows that Cu adsorption was not affected in this pH range but the adsorption of Zn, Mn and Ni was lower at pH 3 compared with pH 4 and 5. Similar adsorption of the metals at pH 4 and 5 was probably due to buffering effects of the peat and at pH 3 high concentrations of H^+ ions lowered metal adsorption by ion exchange. Ringqwist and Öborn[14] reported that the solution pH has minor effect on Cu adsorption on peat but it was one of the main factors affecting Zn adsorption.

Conclusion

(1) The adsorption of the metal ions on to the peat fitted both Langmuir and Freundlich models and the Langmuir model better explained the adsorption. The adsorption capacity of the peat followed the order Cu > Zn > Mn > Ni. (2) The peat

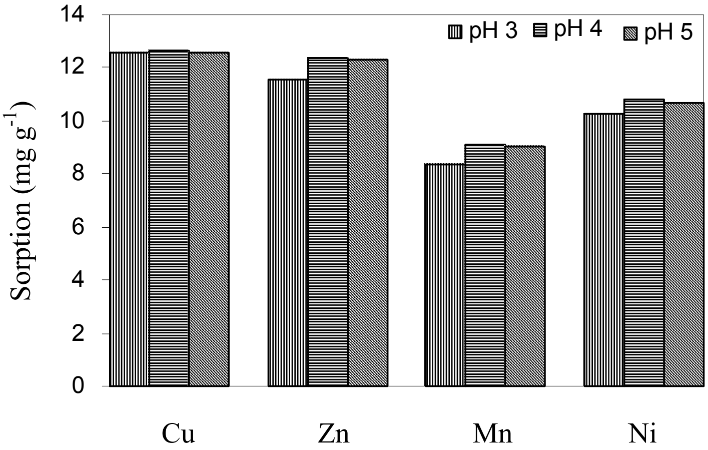

Fig. 8. Effect of initial pH on the sorption of the metal ions for 2×10^{-3} M initial solution concentrations

removed 86-96 % of the metal ions at the lowest initial concentrations and between 68-97 % of the metal ions at the highest initial solution concentration and Cu was the most efficiently removed metal ion in both low and high initial solutions (96 and 97 %). (3) The kinetic study revealed that the adsorption followed the pseudo-second-order model and the interaction between the metal ions and the peat was very fast and equilibrium was reached within 0.5 h. (4) Cu adsorption was not affected in the pH range between 3 and 5 but the adsorption of Zn, Mn and Ni was lower at pH 3 compared with pH 4 and 5.

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