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Removal of Cu(II), Zn(II) and Co(II) ions from aqueous solutions by adsorption onto natural bentonite

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Abstract In this study, the removal of Cu(II), Zn(II) and Co(II) ions from aqueous solutions using the adsorption process onto natural bentonite has been investigated as a function of initial metal concentration, pH and temperature. In order to find out the effect of temperature on adsorption, the experiments were conducted at 20, 50, 75 and 90 °C. For all the metal cations studied, the maximum adsorption was observed at 20 °C. The batch method has been employed using initial metal concentrations in solution ranging from 15 to 70 mg L^{-1} at pH 3.0, 5.0, 7.0 and 9.0. A flame atomic absorption spectrometer was used for measuring the heavy metal concentrations before and after adsorption. The percentage adsorption and distribution coefficients (K_d) were determined for the adsorption system as a function of adsorbate concentration. In the ion exchange evaluation part of the study, it is determined that in every concentration range, adsorption ratios of bentonitic clay-heavy metal cations match to Langmuir, Freundlich and Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm data, adding to that every cation exchange capacity of metals has been calculated. It is shown that the bentonite is sensitive to pH changes, so that the amounts of heavy metal cations adsorbed increase as pH increase in adsorbent-adsorbate system. It is evident that the adsorption phenomena depend on the surface charge density of adsorbent and hydrated ion diameter depending upon the solution pH. According to the adsorption equilibrium studies, the selectivity order can be given as $\mathrm{Zn}^{2+} > \mathrm{Cu}^{2+} > \mathrm{Co}^{2+}$. These results show that bentonitic clay hold great potential to remove the relevant heavy metal cations from industrial wastewater. Also, from the results of the thermodynamic analysis, standard free energy ΔG^0, standard enthalpy ΔH^0 and standard entropy ΔS^0 of the adsorption process were calculated.

Keywords Adsorption · Heavy metals · Bentonite · Removal · Wastewater

1 Introduction

Many toxic heavy metals have been discharged into the environment as industrial wastes, causing serious soil and water pollution. Various physicochemical and biological methods for removal of toxic metal ions have been studied. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive adsorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration. Cost is an important parameter for comparing the adsorbent materials. However, cost information is seldom reported, and the expense of individual adsorbents varies depending on the degree of processing required and local availability. In general, an adsorbent can be assumed as "low cost" if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry. Of course, improved adsorption capacity may compensate the cost of additional processing.

Use of clays as adsorbents to remove contaminants has recently been paid increasing attention because they are readily available, cheap and environmental friendly. An

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ideal heavy metal adsorbent should have a very strong affinity for the target metal, binding it irreversibly under ambient conditions, and simultaneously possessing the ability to release the metal from the structure under different conditions such that the adsorbent can be regenerated for further cleanup. The wide usefulness of clays is a result of their high specific area, high chemical and mechanical stability, and variety of surface and structural properties. The chemical nature and pore structure generally determine the adsorption ability of clays. For gas phase adsorption, pore structure including the nature and volume of pores is a predominant factor. In the case of liquid-phase adsorption, the chemical properties of surface groups influence the extent of adsorption.

Adsorption is the concentration of a substance at the surface or interface (Barrow 1996). The adsorption at a surface or interface is largely as a result of binding forces between atom, molecules, and ions of the adsorbate on the surface (Levine 1995). The commercial adsorbents used today for the removal of heavy metals from solutions include a variety of clays, activated carbon, gels, alumina, silica, zeolites, and other resinous materials (Westrich et al. 1995; Puls and Bohn 1988; Orumwense 1996; Qadeer et al. 1992 and Saleem et al. 1992). Bentonite is a clay consisting essentially of smectite mineral of the montmorillonite group (Grimshaw 1972 and Patterson and Murray 1975). Smectite group clays such as bentonite posses a net negative structural charge resulting from isomorphic substitution of cations in crystal lattice. This negative charge is neutralized by the adsorption of positively charged species, giving clay the ability to attract and hold cations such as toxic heavy metals. Due to this negative charge, bentonite clays have little affinity for anionic species such as that of hexavalent chromium depending upon medium pH. In aqueous solutions, water is intercalated into the interlamellar space of montmorillonite, leading to an expansion of the minerals. Since smectite clays are swelling in nature, today these naturally available clays have also been used for adsorption removal of anions and organic toxic materials by entering and fixing a large cationic species like hexadecyltrimethylammonium cation, HDTMA$^+$ in the interlayer regions of montmorillonite (Zhang et al. 1993). Bentonite has a variety of uses in industry; it is used as an emulsifying agent for asphaltic and resinous substances, as an adhesive agent in horticultural sprays and insecticides, in concrete mixtures, and as a plasticizer in ceramic bodies. It is also used in refining oils and fats, drilling mud, foundry sands, in some detergents and others (Blackman 1969).

Bentonite as an adsorbent for the removal of malathion (Pradas et al. 1993), Sr(II) (Khan et al. 1995a), UO_2^{2+} ion (Olguin et al. 1997), and Cd(II) and Pb(II) under estuarine and seawater conditions (Kozar et al. 1992), Cu(II) (Rauf et al. 1999), Cr(III) (Ikram et al. 2002), Pb(II) (Naseem and Tahir 2001), Pb(II) and Ni(II) (Lee et al. 2000), Zn(II) (Mellah and Chegrouche 1997), and Pb(II), Cu(II), and Zn(II) (Bereket et al. 1997) from aqueous solutions has already been reported in the literature.

Due to be rapidly available and inexpensive clay mineral in Turkey, the present study is undertaken with the following specific objectives:

1. to examine the performance and effectiveness of bentonite in removal of Cu^{2+}, Zn^{2+} and Co^{2+} ions by adsorption from aqueous solution;
2. to determine the effect of initial metal concentration, pH and temperature on the adsorption capacity of the bentonitic clay as an adsorbent;
3. to study the applicability of the Langmuir, Freundlich and DKR isotherms;
4. to provide additional information on the adsorption of the relevant heavy metal cations by the bentonitic clay; and
5. to understand the mechanism of adsorption of the relevant metal cations by the clay based on parameters such as adsorbent capacity, free energy change, enthalpy change and entropy change.

2 Experimental

2.1 Bentonite as an adsorbent source

The raw bentonite sample used in this study was received from the mine beds in Kütahya Region in Turkey whose basic clay mineral is calcium-montmorillonite, was used in the adsorption experiments. It was air-dried and passed through a 200-µm sieve. The amounts of metals available in the clay were considered as percentage metal oxide amounts. The percentage of volatile components, on condition of fact that almost all of them are water, was called as ignition loss. After a sample having a certain mass taken from the clay of whose carbonate and moisture was removed, was heated and dried for 2 hours at 110 °C; the decrease in mass of the sample was considered as ignition loss. The complete chemical composition of metal oxides in the clay sample remained, was determined as follows: 71.90% SiO_2, 13.85% Al_2O_3, 0.68% Fe_2O_3, 0.09% TiO_2, 2.42% CaO, 1.27% MgO, 0.39% Na_2O, 1.62% K_2O and 7.50% ignition loss. In order to determine the pH-dependent CEC values of bentonite sample, 3 g/100 g bentonite suspensions containing 0.01 M NaCl were prepared at three different pH values, pH 8.0, pH 6.35 and pH 5.0 where adsorbent surface hold negative, zero and positive charges, respectively. The pH values of suspensions were adjusted with adding estimated amounts of 1 M NaOH or HCl solutions. The pH values of well-homogenized suspensions were measured, and then all were stored vials for three days. The equilibrium pH values of suspensions were measured before the ECEC measurements. The pH shift during standing of three days was about 0.2-pH unit. Here, the cation exchange capacity (CEC) of clay is simply a measure of the quantity of sites on clay surfaces that can retain positively charged ions (cations) by electrostatic forces. The CEC is defined as the sum of positive charges of adsorbed cations that clay can adsorb at a specific pH. The CEC is expressed as centimoles of positive charge per gram (cmol kg^{-1}), of oven dry clay or meq per 100 g clays. The effective cation exchange capacity (ECEC or $\mathrm{CEC}_{\mathrm{eff}}$.), as the sum of the basic exchangeable cations and extractable Al, is a useful parameter to estimate cation exchange capacity in clays which don't contain salts and carbonates in the clays containing pH-dependent charge.

2.2 Reagents and apparatus

Merck firm supplied inorganic chemicals as analytical-grade reagents and doubly distilled water were used. The heavy metal cations studied were Cu(II), Zn(II) and Co(II). We prepared a synthetic stock solution of copper, zinc and cobalt using their nitrate salts, $\mathrm{Cu(NO_3)_2{\cdot}3H_2O}$, $\mathrm{Zn(NO_3)_2{\cdot}6H_2O}$ and $\mathrm{Co(NO_3)_2{\cdot}6H_2O}$, respectively, in doubly-distilled water. The diluted NaOH and HCl solutions (0.01 M or 0.1 M) were used in order to adjust the desired pH values of solutions.

To determine the concentrations of the heavy metals remained in the equilibrium solutions, a Unicam 929 atomic absorption spectrophotometer was used. The pH measurements were made with a pM-meter, model Henna pH 211. The intensive mixing (350 rpm) of the adsorbent particles in the aqueous phase was performed by using a temperature controlled-water bath with shaker. Additionally, a desiccator and other glasswares were used for drying and all of the adsorption studies.

2.3 Batch adsorption studies

The adsorption of heavy metals on bentonite was carried out using the batch method. Batch adsorption experiments were conducted using 300 mg of adsorbent with 100 mL of solutions containing heavy metal ions of desired concentrations at different temperatures (20, 50, 75 and 90 °C) and pH values (3.0, 5.0, 7.0 and 9.0) in 100 mL glass stoppered flasks. The pH of solutions was adjusted by using dilute NaOH or HCl solutions before adsorption analysis. The flasks were shaken in a temperature-controlled water bath for 30 min with the mixing rate of 350 rpm and the solutions containing heavy metals were filtered through Whatman filter paper (No. 42) after the contact time of 30 min. The exact concentration of metal ions and filterable metal concentrations were determined by AAS. The flame type was air-acetylene and adsorption wavelengths are Cu^{2+} (324.7 nm), Zn^{2+} (213.9 nm), and Co^{2+} (240.7 nm). The percent adsorption (%) and distribution ratio (K_d) were calculated using the equations

$$\%\ \text{Adsorption} = \frac{C_\mathrm{i} - C_\mathrm{f}}{C_\mathrm{f}} \times 100, \tag{1}$$

where C_i and C_f are the concentrations of the metal ion in initial and final solutions, respectively, and

$$K_\mathrm{d} = (\text{amount of metal ion in adsorbent})/ \\ (\text{amount of metal ion in solution}) \times V/m\ (\text{mL/g}), \tag{2}$$

where V is the volume of the solution (mL) and m is the weight of the adsorbent (g). The percent adsorption and K_d (mL/g) can be correlated by the following equation (Khan et al. 1995b):

$$\%\ \text{Adsorption} = \frac{100K_\mathrm{d}}{K_\mathrm{d} + V/m}. \tag{3}$$

3 Results and discussion

3.1 The physicochemical properties of bentonite

The chemical analysis was performed with Unicam 929 atomic absorption spectrometer. The specific surface area of the bentonite calculated from the methylene blue adsorption method was 54.14 m^2/g (Barton 1987). The effective cation exchange capacity was determined by the method of Juo et al. (Jou et al. 1976). It involves the summation of the exchangeable acidity and the cation exchange capacity of the adsorbent. The pH value of water saturated bentonitic clay paste was practically 6.35 while its point of zero charge (pzc) being the pH of adsorbent suspension at which its surface has a net charge of zero was 6.50. By using this technique, total exchange capacity values at pH 5.0, 6.35 and 8.0 for adsorbent were determined as the summation of exchangeable cations (Ca + Mg + K) and exchangeable acidity (Al + H). Exchangeable bases were displaced with 1 N $\mathrm{CH_3COONH_4}$ and the cations were determined by atomic absorption spectroscopy, while the exchangeable acidity was displaced by 1 N KCl and titrated with 0.1 N NaOH the first permanent end point using phenolphthalein indicator. The ECEC values and cation composition of the exchange sites as related to the adsorbent pH values were as follows:

pH	meq/100 g clay		
	Exchangeable acidity	Basic cations	Total CEC or ECEC
5.0	11.67	33.83	45.50
6.35	7.25	44.60	51.85
8.0	3.45	58.95	62.40

At pH 8.0, the ECEC value increased markedly with increasing pH value because of its dependence on pH. This pH dependence, particularly in adsorbent, is most likely related to blockage of exchange sites by Fe and Al at more acidic pH values or due to protons being strongly held at low pH. At pH 5.0, due to the relatively high clay content of the studied adsorbent, a large proportion of the pH-dependent CEC may have been derived from the decrease in the surface charge density of adsorbent with decreasing pH value. As a result, pH contributes to CEC as dissociation of functional groups such as silanol and aluminol groups at pH > 6.35 increases the number negatively charged sites; in addition a decrease in CEC value at low pH might be related to blockage of exchange sites by Fe and Al. When these ECEC values were compared to the adsorption values of the relevant heavy metal cations, it is clearly appeared that how the pH-dependent ion exchange mechanism entering into play in this interfacial system is important in terms of the elucidation of the adsorption mechanism. It was found that Kütahya bentonite contains Ca-montmorillonite as the basic clay mineral as well as some illite as another clay mineral and some opal-CT (Miles 1994) as a non-clay mineral by XRD analysis.

3.2 Adsorption of heavy metals on bentonite

The adsorption of Cu^{2+}, Zn^{2+} and Co^{2+} ions onto bentonite as a function of their concentrations, pHs and temperatures was studied at different pH values and temperatures by varying the metal concentration from 15 to 70 mg/L while keeping all others parameters such as particle size, contact time, ionic strength and adsorbent to adsorbate ratio constant. Throughout the adsorption experiments, shaking period was considered as 30 min in each experiment while a bentonite sample of 300 mg was used as an adsorbent source.

3.2.1 *Effect of the initial metal concentration*

As can be seen in Fig. 1 and Table 1, adsorption capacity of bentonite has linearly increased with the concentration of metal ions when the concentrations of metal ions increased to 50 mg/L and at the high concentrations, it was observed the adsorption didn't change with metal ion concentration. These results indicate that the pores of clay minerals filled after a certain period and after that, to increase metal concentration didn't make a considerable effect on adsorption. These results indicate that energetically less favourable sites become involved with increasing metal concentrations in the aqueous solution. The heavy metal sorption is attributed to different mechanisms of ion-exchange processes as well as to the adsorption process. During the possible ion-exchange process, firstly metal ions may move through either the pores of the bentonite mass or through channels of the crystal lattice. Secondly, they may replace exchangeable cations, mainly such as sodium, magnesium and calcium. Diffusion may also occur by slowly or fastly passing the metal ions through the adsorbent pores, but diffusion might be retarded at which the metal ions or hydrated metal ions couldn't pass through the smaller diameter channels. In this case, the metal ion sorption could mainly be attributed to ion-exchange reactions in the microporous minerals of the bentonite samples. Figure 2(a) and (b) shows distribution coefficients (K_d) as a function of metal ions concentrations. The K_d values increase with the decreasing concentration of metal ions. In other words, the K_d values increase as dilution of metal ions in solution proceeds.

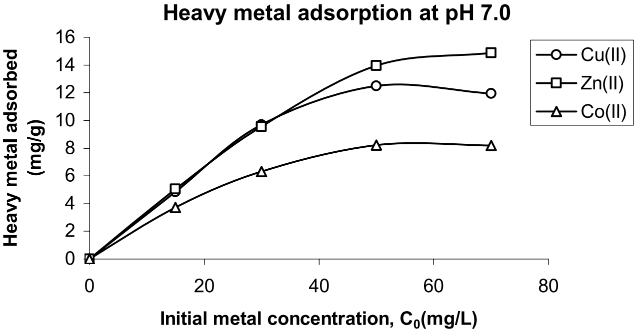

Fig. 1 Adsorption of heavy metal ions prepared at different concentrations in aqueous solution on bentonite at pH 7.0 and 20 °C

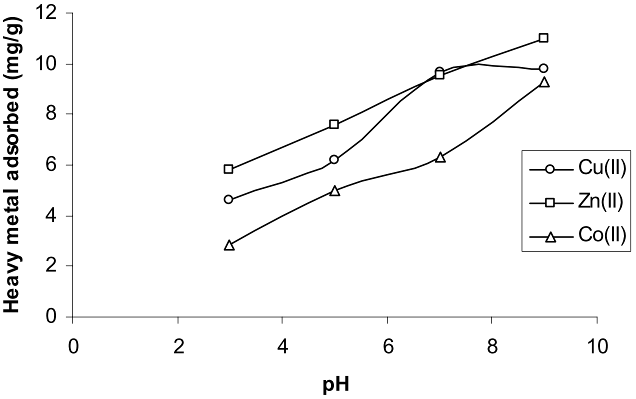

Fig. 2 pH effect on the adsorption of heavy metal ions having initial concentrations of 30 mg/L on bentonite at room temperature of 20 °C

These results indicate that energetically less favorable sites become involved with increasing metal concentration in the aqueous solution. The maximal exchange levels or maximum adsorptions attained were as follows: Cu^{2+} 99.48%, Zn^{2+} 100%, and Co^{2+} 88.13% at pH 9.0 and 20 °C while they are Cu^{2+} 95.60%, Zn^{2+} 100%, and Co^{2+} 73.24% at pH 7.0 and 20 °C.

3.2.2 *Effect of solution pH*

The effect of solution pH on heavy metal adsorption onto bentonite in single metal system was also studied in the

Table 1 The amounts adsorbed and adsorption percentages of the heavy metal ions on bentonite from aqueous solution in the pH range investigated at 20°

Initial concentration (ppm)	Cu^{2+} ion		Zn^{2+} ion		Co^{2+} ion	
	Adsorbed (ppm)	% Adsorption	Adsorbed (ppm)	% Adsorption	Adsorbed (ppm)	% Adsorption
at pH 3.0						
16.87	9.52	56.45	10.08	59.76	5.52	32.72
29.48	13.89	47.13	17.34	58.82	8.50	28.82
47.15	21.31	45.19	26.46	56.11	12.79	27.12
60.53	22.81	37.69	27.08	44.74	12.11	20.00
at pH 5.0						
14.83	10.50	70.80	11.12	75.00	7.76	52.35
30.78	18.51	60.15	22.81	74.10	14.98	48.68
48.57	28.26	58.18	35.76	73.62	18.24	37.56
62.23	29.32	47.12	37.70	60.57	18.81	30.22
at pH 7.0						
15.17	14.50	95.60	15.12	100	11.11	73.24
29.05	24.60	84.70	28.63	98.56	18.93	65.18
45.01	37.41	83.12	41.88	93.05	24.63	54.73
57.22	35.84	62.63	44.59	77.92	24.52	42.86
at pH 9.0						
15.01	14.93	99.48	14.95	100	13.23	88.13
33.08	29.28	88.52	32.99	99.72	27.87	84.26
48.98	43.26	88.33	47.48	96.93	41.03	83.78
61.74	45.47	73.65	50.70	82.12	41.38	67.03

The adsorption equilibrium data measured at temperatures of 50, 75 and 90 °C weren't given in terms of the applicability of heavy metals removal from aqueous solution by adsorption

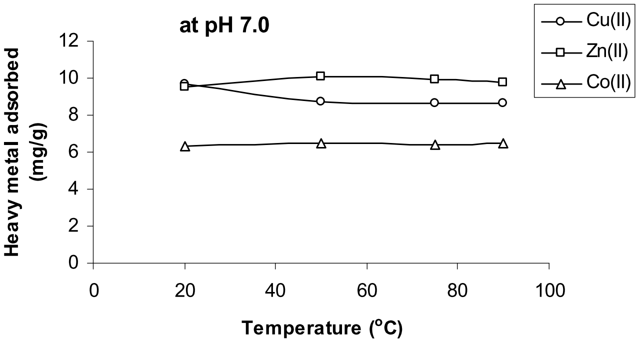

Fig. 3 Temperature effect on the adsorption of heavy metal ions having the initial concentrations of 30 mg/L on bentonite at pH 7.0

pH range from 3.0 to 9.0; the results are shown in Fig. 3. From Fig. 3, as the initial pH value increased, the adsorption of metals by bentonite also increased. This case can be explained by its point of zero charge (pzc). The pzc of an adsorbent is the pH of adsorbent suspension at which its surface has a net charge of zero (Sparks 1995). If the measured pH of the colloid system is less than the pzc, there is competition from H^+ ions for surface complexation sites on clay surfaces and the surfaces have net positive charges. Oppositely, if the pH is higher than the pzc, the net change is negative. Surfaces with negative charges attract metal cations in the solutions. The change in H^+ and OH^- ions in solution will cause the surface functional groups and clay minerals to protonate and deprotonate by adsorption of H^+ or OH^- ions, respectively, as shown in (4)–(5) below

$$\equiv\text{Si–OH} + H^+ \rightarrow \equiv\text{Si–OH}_2^+ \tag{4}$$

$$\equiv\text{Si–OH} + OH^- \rightarrow \equiv\text{Si–O}^- + H_2O \tag{5}$$

The bentonite used in this study has experimentally *a* pzc of 6.35. Therefore, at a pH value above its pzc, the net charge on bentonite becomes negative while at a pH value below its pzc the net surface charge becomes positive and according to (5), the negative charges increase with the increase in the solution pH. Therefore, the adsorbent gains a high charge resulting from the spread of isomorphous substitution in tetrahedral and octahedral sheets for bentonite. It should be also noted that the clay sample has a higher adsorption affinity to adsorb metal cations at high pH values. Figure 3 shows the plots of K_d versus pH. The pH was observed to be an important factor affecting the adsorption of copper, zinc and cobalt ions on bentonite. K_d increased with increasing pH and, in particular, had a sharp increase at pH higher than 7.0. This trend may be explained in the following three ways. Firstly, it is related to the change of surface charge of bentonite particles. The surface charge increases negatively with increasing solution pH, which results in the increase in K_d values (Jeong et al. 1995; Heyes and Lockie 1987). That is, the higher negative surface charge allows the relevant metal ions (Zn^{2+}, Cu^{2+} and Co^{2+}) to have easier electrostatic reaction with the bentonite particles. Secondly, it is due to a competitive ion-exchange reaction at low pH. The metal ions compete with H^+ ions for the available sorption sites, giving a reduction of their K_d values. The contribution of ion competition, however, will decrease with increasing pH. Thirdly, a sharp increase in K_d at pH 9.0 may be due to precipitation or formation of complexation products of metal ions by hydrolysis. As a matter of fact, increasing pH was reported to increase the adsorption of metal ions from kaolinite suspensions (Jeong et al. 1995). Gutierrez and Fuentes (1993) studied the adsorption behaviour of Sr, Cs and Co by Ca-montmorillonite and showed that Co adsorption increase above the pH of precipitation of $Co(OH)_2$. In another study (Kara et al. 2003), in order to be clarified the adsorption mechanism of Co^{2+} ions on natural sepiolite, the release pattern of Mg^{2+} and Co^{2+} ions were simultaneously followed. The released Mg^{2+} ion concentration against pH in the absence and presence of Co^{2+} ions were measured to identify the effect of Co^{2+} ions on the solubility of Mg^{2+} ions. As a result, in the pH range of 5.0–8.2, it was found that the adsorption was based on the ion-exchange mechanism. At pH values higher than 8.2, it was concluded that ion-exchange mechanism was not indicative due to the hydrolysis of Co^{2+} ions as insoluble complexes.

3.2.3 *Effect of temperature*

The single metal adsorption isotherms onto bentonite were conducted at temperatures of 20, 50, 75 and 90 °C. As can be seen in Figs. 4a and 4b, it was observed that the medium temperature indicated a negative effect on adsorption of metal ions. Metal ion adsorption has decreased with increasing the temperature. Metal ions adsorbed on the clay surface may be released into the aqueous solution because the saturation degree of solutions heated, decreased due to desorption of metal cations from the clay surface. In fact, this case may arise from the increasing desorption tendency of adsorbate ions from the interface to solution with increasing temperature. The adsorption of metal cations was found to decrease with increasing temperature, indicating that metal adsorption on the adsorbent surface was favored at lower temperatures. The metal adsorption percent followed the order 20 °C > 50 °C > 75 °C > 90 °C. The decrease in adsorption with increasing temperature indicated the exothermic nature of the adsorption process.

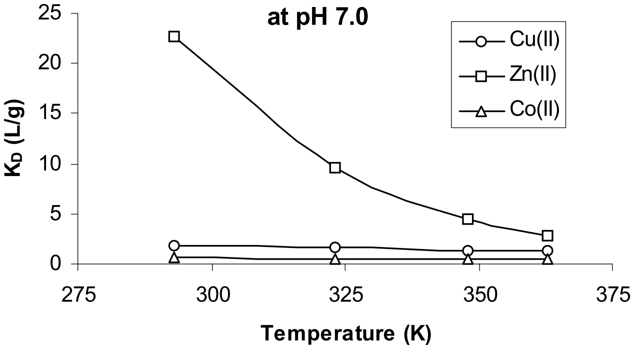

Fig. 4a Plot of distribution coefficient, K_D against temperature for Cu^{2+}, Zn^{2+} and Co^{2+} ions on the adsorption of heavy metal ions having the initial concentrations of 30 mg/L onto bentonite at pH 7.0

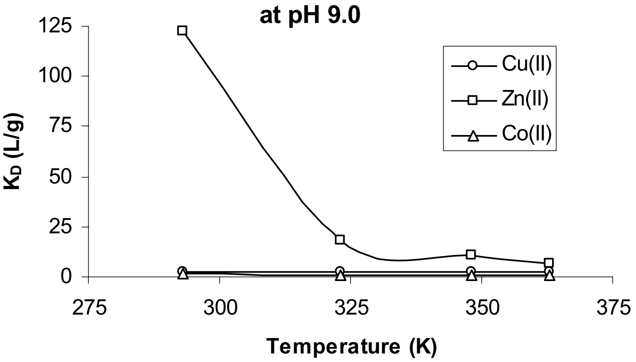

Fig. 4b Plot of distribution coefficient, K_D against temperature for Cu^{2+}, Zn^{2+} and Co^{2+} ions on the adsorption of heavy metal ions having the initial concentrations of 30 mg/L onto bentonite at pH 9.0

3.3 Isotherm models

An adsorption isotherm is a good tool for understanding the nature of a surface. However, a correct selection of adsorption equation for different concentration ranges reveals a true picture of the surface. At low coverage, Henry and Freundlich models explain the adsorption process, whereas the Langmuir model describes the monolayer coverage at high concentrations (Thomas and Thomas 1967). The Dubinin-Radushkevich (D-R) isotherm explains multilayer formation in microporous solids. The Dubinin-Kaganer-Radushkevich (DKR) equation confines to the monolayer region in micropores and has been widely used to explain energetic heterogeneity of solid surfaces at low coverages.

The adsorption data have been subjected to different adsorption isotherms, namely, Langmuir, Freundlich and Dubinin-Kaganer-Radushkevich (DKR). The equilibrium data for metal cations over the concentration range from 15

Table 2 Langmuir and Freundlich constants for the adsorption of heavy metal cations on bentonite at different pH values and 20 °C

pH	Metal cation	Langmuir constants				Freundlich constants		
		Q_0 (mg/g)	b (L/mg)	R^2	R_L	K_f (mg/g)	$1/n$	R^2
3.0	Cu^{2+}	12.376	0.044	0.9752	0.244	1.020	0.568	0.9861
	Zn^{2+}	15.674	0.046	0.9424	0.236	1.100	0.655	0.8897
	Co^{2+}	6.775	0.036	0.9465	0.286	0.460	0.590	0.9594
5.0	Cu^{2+}	14.104	0.075	0.9804	0.161	1.622	0.540	0.9803
	Zn^{2+}	21.097	0.069	0.9354	0.172	1.732	0.672	0.9484
	Co^{2+}	8.467	0.074	0.9883	0.162	1.093	0.491	0.9504
7.0	Cu^{2+}	12.547	1.140	0.9980	0.012	5.755	0.285	0.9417
	Zn^{2+}	15.060	5.228	0.9999	0.003	10.063	0.198	0.9664
	Co^{2+}	9.911	0.168	0.9950	0.078	2.290	0.396	0.9591
9.0	Cu^{2+}	15.924	1.005	0.9904	0.014	8.482	0.215	0.9704
	Zn^{2+}	17.065	9.607	0.9999	0.002	12.320	0.187	0.8225
	Co^{2+}	16.863	0.255	0.9851	0.053	3.834	0.488	0.9249

to 70 mg/L at 20 °C have been correlated with the Langmuir isotherm (Langmuir 1918):

$$C_e/C_{ads} = 1/Q_0 b + C_e/Q_0, \tag{6}$$

where C_e is the concentration of metal ion solution (mg/L) at equilibrium and C_{ads} is the amount adsorbed onto adsorbent at equilibrium (mg/g). The constant Q_0 signifies the adsorption capacity (mg/g) and b is related to the energy of adsorption (L/mg). Maximum adsorption capacity (Q_0) represents monolayer coverage of adsorbent with adsorbate and b represents enthalpy of adsorption and should vary with temperature. A linear plot is obtained when C_e/C_{ads} is plotted against C_e over the entire metal concentration range studied. The Langmuir model parameters and the statistical fits of the adsorption data to this equation are given in Table 2. The Langmuir model effectively described the adsorption data with all R^2 values >0.9354. According to the Q_0 (mg/g) parameter, adsorption on bentonite is produced following the sequence $Zn^{2+} > Cu^{2+} > Co^{2+}$ at pH 3.0, 5.0 and 7.0 while the selectivity sequence is $Zn^{2+} > Co^{2+} > Cu^{2+}$ at pH 9.0. The high Si/Al mole ratio of bentonite results in a low anionic field that gives rise to a good selectivity. However, at high pH values since the surface charge density will be more negative, the adsorption of the easily hydrolysable metal cations such as Zn^{2+} and Co^{2+} will also increase. As a result, at pH 9.0 the selectivity sequence of metal cations was changed in the order $Zn^{2+} > Co^{2+} > Cu^{2+}$ due to have the more amphoteric properties of Zn^{2+} and Co^{2+} ions according to Cu^{2+} ion.

The Freundlich adsorption isotherm, one of the most widely used mathematical descriptions, usually fits the experimental data over a concentration range of 15–70 mg/L. This isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The Freundlich adsorption isotherms were also applied to the removal of Zn^{2+}, Cu^{2+} and Co^{2+} ions onto bentonite,

$$\ln C_{ads} = \ln K_f + \frac{1}{n} \ln C_e, \tag{7}$$

where C_e is the equilibrium concentration in mg/L and C_{ads} shows that the adsorption seems to follow the Freundlich isotherm model as well as Langmuir isotherm. The constants K_f and $1/n$ were calculated for each cation (Table 2). K_f is a parameter related to the temperature and n is a characteristic constant for the adsorption system under the study. Values of n between 2 and 10 show good adsorption. The numerical value of $1/n < 1$ indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations. This isotherm does not predict any saturation of the adsorbent by the adsorbate; thus infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface (Hasany et al. 2002). In order to predict whether the adsorption process by bentonite is favourable or unfavourable for the Langmuir type adsorption process, the isotherm shape can be classified by a term "R_L", a dimensionless constant separation factor, which is defined below (Altındoğan et al. 2000 and Rao et al. 2002):

$$R_L = \frac{1}{1 + bC_e}, \tag{8}$$

where R_L is dimensionless separation factor, C_e is the equilibrium concentration or the highest initial concentration of the metal cation (mg/L) in the investigated concentration range and b is Langmuir constant (L/mg). The parameter R_L indicates the shape of the isotherm accordingly:

Table 3 Dubinin-Kaganer-Radushkevich constants for the adsorption of heavy metal cations on kaolinite at different pH values and 20 °C

pH	Metal cation	Dubinin-Kaganer-Radushkevich constants			
		X_m (mg/g)	Sorption energy, E (kJ/mol)	Regression equation	R^2
3.0	Cu^{2+}	7.037	0.229	$\ln C_{ads} = 1.9583 - 8.7638\varepsilon^2$	−0.9274
	Zn^{2+}	9.282	0.325	$\ln C_{ads} = 2.2281 - 9.3600\varepsilon^2$	−0.9824
	Co^{2+}	4.237	0.159	$\ln C_{ads} = 1.4438 - 20.4227\varepsilon^2$	−0.9644
5.0	Cu^{2+}	8.955	0.328	$\ln C_{ads} = 2.19212 - 3.7671\varepsilon^2$	−0.9415
	Zn^{2+}	12.307	0.640	$\ln C_{ads} = 12.5102 - 3.6494\varepsilon^2$	−0.9765
	Co^{2+}	6.320	0.179	$\ln C_{ads} = 1.8437 - 8.6687\varepsilon^2$	−0.9977
7.0	Cu^{2+}	10.932	0.850	$\ln C_{ads} = 2.3917 - 0.1669\varepsilon^2$	−0.9183
	Zn^{2+}	13.415	5.351	$\ln C_{ads} = 2.5964 - 0.0183\varepsilon^2$	−0.9685
	Co^{2+}	8.061	0.345	$\ln C_{ads} = 2.0870 - 2.7562\varepsilon^2$	−0.9831
9.0	Cu^{2+}	12.932	3.716	$\ln C_{ads} = 2.5597 - 0.0238\varepsilon^2$	−0.9261
	Zn^{2+}	17.288	9.709	$\ln C_{ads} = 2.8500 - 0.0207\varepsilon^2$	−0.9147
	Co^{2+}	13.191	0.744	$\ln C_{ads} = 2.5795 - 0.9456\varepsilon^2$	−0.9730

$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$R_L < 1$	Favourable
$R_L = 0$	Irreversible

It was found that the calculated R_L values for Cu^{2+}, Zn^{2+} and Co^{2+} adsorption onto bentonite were 0.012, 0.003 and 0.078 at 20 °C and pH 7.0, respectively. These values indicate that the Cu^{2+}, Zn^{2+} and Co^{2+} adsorption processes are highly favourable at the highest initial metal concentrations of 70 mg/L, 20 °C and pH 7.0.

The DKR adsorption isotherm has also been used to describe the adsorption of metal ions on bentonite. The DKR equation has the form

$$\ln C_{ads} = \ln X_m - \beta\varepsilon^2, \tag{9}$$

where C_{ads} is the amount of metal ions adsorbed per unit weight of adsorbent (mg/g), X_m is the maximum adsorption capacity, β is the capacity coefficient related to mean adsorption energy, and ε is the Polanyi potential, which is equal to

$$\varepsilon = -RT \ln\left(1 + \frac{1}{C_e}\right), \tag{10}$$

where R is the gas constant (J/mol·K) and T is the temperature (K). The saturation limit, X_m may represent the total specific micropore volume of the adsorbent. The adsorption potential is independent of the temperature but varies according to the nature of adsorbent and adsorbate (Khan et al. 1995b). The slope of the plot of $\ln C_{ads}$ versus ε^2 gives β (mol^2/J^2) and the intercept yields the adsorption capacity, X_m (mg/g). The adsorption space in the vicinity of a solid surface is characterized by a series of equipotential surfaces having the same adsorption potential. This adsorption potential is independent of the temperature but varies according to the nature of adsorbent and adsorbate. The adsorption energy also worked out by using the following relationship:

$$E = \frac{1}{\sqrt{-2\beta}}. \tag{11}$$

The plot of ln C_{ads} against ε^2 for metal ions adsorption on bentonite was withdrawn with the statistic of linear regression. The DKR parameters are calculated from the slope and intercept of the straight line obtained by the way and listed in Table 3. As shown in Table 3, the mean adsorption energy values are 9.709 for Zn^{2+}, 3.716 for Cu^{2+} and 0.744 kJ/mol for Co^{2+} on bentonite at pH 9.0 and 20 °C while they are 5.351 for Zn^{2+}, 0.851 for Cu^{2+} and 0.345 kJ/mol for Co^{2+} at pH 7.0 and 20 °C. These values are of the orders expected of an ion exchange mechanism for Zn^{2+} ion and Zn^{2+}-Cu^{2+} ion-pair at pH 7.0 and 9.0, respectively, in which the adsorption energy lies within 8–16 kJ mol^{-1} (Helfferich 1962). However, the E value is lower than the order expected of an ion-exchange mechanism for Co^{2+} ions. Perhaps this low value is due to fact that cobalt is weakly bound to the clay surface in the neutral or alkaline pH range. The adsorption capacity, X_m in the DKR equation is found to be 17.288 for Zn^{2+}, 13.191 for Co^{2+} and 12.932 mg/g for Cu^{2+} at pH 9.0 and 20 °C while it is 13.415 for Zn^{2+}, 10.932 for Cu^{2+} and 8.061 mg/g for Co^{2+} at pH 7.0 and 20 °C. The adsorption capacity X_m at the DKR region is calculated to be 13.415 mg g^{-1} for the adsorption of zinc ions at pH 7.0, which is less than the adsorption capacity observed at the Langmuir region. The DKR equation is apparently obeyed in a lower concentration range.

Table 4 The thermodynamic parameters for the adsorption of Cu^{2+}, Zn^{2+} and Co^{2+} ions on bentonite at different pH values as a function of medium pH

Metal ion	ΔH^0 (J/mol)	ΔG^0 (J/mol)				ΔS^0 (J/mol·K)			
		20 °C	50 °C	75 °C	90 °C	20 °C	50 °C	75 °C	90 °C
at pH 3.0									
Cu^{2+}	12.562	7592.53	7475.95	8273.31	5534.38	−25.87	−23.11	−23.74	−15.21
Zn^{2+}	7.937	7484.86	8188.12	7592.52	7446.87	−25.52	−25.33	−21.79	−20.49
Co^{2+}	−1.777	8131.86	9443.56	9699.41	10748.24	−27.76	−29.24	−27.88	−29.61
at pH 5.0									
Cu^{2+}	−3.571	6319.72	8357.84	8012.63	9034.93	−21.58	−25.89	−23.04	−24.90
Zn^{2+}	−4.442	6512.89	7586.58	8054.58	9426.97	−22.24	−23.50	−23.16	−25.98
Co^{2+}	6.113	6349.20	5879.19	5192.27	7003.83	−21.65	−18.18	−14.90	−19.28
at pH 7.0									
Cu^{2+}	−21.029	−319.60	2356.73	5696.85	3489.09	1.02	−7.36	−16.43	−9.67
Zn^{2+}	−17.722	−4029.39	2791.50	148.14	−1762.50	13.69	8.59	−0.48	4.81
Co^{2+}	0.659	4339.49	4615.43	4970.93	5229.26	−14.81	−14.29	−14.28	−14.40
at pH 9.0									
Cu^{2+}	−10.222	−11.69	177.24	1302.55	2576.75	0.005	−0.58	−3.77	−7.13
Zn^{2+}	−24.387	−5511.45	−3601.15	−2412.12	−740.91	18.73	12.21	6.86	1.97
Co^{2+}	−12.344	3236.85	3861.64	5194.00	7450.19	−11.39	−11.99	−14.96	−20.56

3.4 Adsorption thermodynamics

In order to explain the effect of temperature on the adsorption thermodynamic parameters, standard free energy ΔG^0, standard enthalpy ΔH^0 and standard entropy ΔS^0 were determined. To calculate the values of the parameters the following equations were used:

$$\ln\left(\frac{1}{b}\right) = \frac{\Delta G^0}{RT} \qquad \text{or} \qquad \ln b = -\frac{\Delta G^0}{RT} \tag{12}$$

$$\ln b = \ln b_0 - \frac{\Delta H^0}{R} \cdot \frac{1}{T} \tag{13}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0, \tag{14}$$

where b is the Langmuir constant that is related with the energy of adsorption, b_0 a constant, R the ideal gas constant and T is the absolute temperature (K). The calculated values of thermodynamic parameters ΔG^0, ΔS^0 are given in Table 4. It can be stated that the Cu^{2+} and Zn^{2+} adsorptions on bentonite are an exothermic phenomenon from the calculated ΔH^0 values of -21.027 and $-17.722\ \mathrm{J\,mol^{-1}}$ at pH 7.0 while the Co^{2+} adsorption on bentonite is an endothermic phenomenon by a ΔH^0 value of $0.659\ \mathrm{J\,mol^{-1}}$ in the temperature range investigated. The value of ΔH_{ads} is less than $40\ \mathrm{kJ\,mol^{-1}}$, indicating that adsorption process is physical in nature. Its magnitude shows that there is a strong or weak interaction between adsorbent and adsorbate. The enthalpy change (ΔH^0) was determined graphically plotting $\ln b$ versus $1/T$, which is a straight line. The values of free energy (ΔG^0) and entropy (ΔS^0) calculated numerically from Langmuir isotherm data by means of ΔG^0 and ΔS^0 depending on ln b are presented in Table 4. It can be stated that the Cu^{2+}, Zn^{2+} and Co^{2+} ions adsorption on bentonite is an exothermic phenomenon from the calculated ΔH^0 values of -10.222, -24.387 and $-12.344\ \mathrm{J\,mol^{-1}}$ at pH 9.0. The negative Gibbs' free energy values confirm the feasibility of the adsorption process and that adsorption is spontaneous for Cu^{2+} and Zn^{2+} ions at pH 7.0, 9.0 and 20 °C. The positive Gibbs' free energy values imply that adsorption is non-spontaneous for Co^{2+} ion at pH 7.0, 9.0 and 20 °C. Also, these values imply that the retention process of Cu^{2+} and Zn^{2+} ions by the clay is a combination of two mechanisms: ions exchange and adsorption. The increase in free energy change with the rise in temperature shows an increase in feasibility of adsorption at higher temperatures for Zn^{2+} ion at pH 7.0 and 9.0. The decrease in ΔG^0 with decreasing temperature shows that the adsorption reaction is more favourable at lower temperatures. At lower temperatures, the metal ions are readily adsorbed due to the high adsorption rate in equilibrium and hence their adsorption becomes more favourable at lower temperatures. A good correlation can be observed with the calculated thermodynamic parameters and in the decreased percentage adsorption with increasing temperature. Entropy has been defined as the degree of chaos of the system and the negative value of this parameter found in our study reflects the adsorption of Co^{2+} ion at the all pH values investigated. During the adsorption process, the Co^{2+} ions become associated on the surface of the adsorbent resulting in the loss of degree of freedom and thus explaining the decrease in the value of this parameter. The positive values of entropy may be due to some structural changes in both the adsorbent and adsorbate during the adsorption process for Cu^{2+} and Zn^{2+} ions at pH 7.0 and 9.0. An other possible explain may be due to the strongly binding or fixation of these metal ions onto the active sites of the clay surface at specifically pH 7.0 and 9.0 pH. The entropy value for the adsorption of metal ions in low pH values was found to be negative. This is explained as due to the fact that there is a competition from H^{+} ions in solution phase for surface complexation sites on clay surfaces. The positive change in entropy value for the adsorption of metal ions in high pH values can be described to the increasing negative charge of the clay surface being responsible for electrostatic adsorption. Assuming charged ions to be present in the water, different binding mechanisms can be plausible at the clay mineral–water interface. For a clay surface being negatively charged a counterlayer of positively charged metal cations from the surrounding solution is formed due to electrostatic attraction of opposite charges, i.e., reversible electrostatic processes. Thus, a diffuse layer of non-specifically adsorbed cations from the water adjacent to the clay surface is formed. Some of these counterions may approach the surface more closely to form weak outer-sphere surface complexes (primarily through electrostatic binding or ion pairing) or stronger inner-sphere surface complexes (primarily through chemical bonding), i.e., irreversible chemical adsorption processes (if the chemical adsorption is predominant in equilibrium).

4 Conclusions

It has been observed that natural bentonite is a good material, which can adsorb heavy metals such as Cu^{2+}, Zn^{2+} and Co^{2+} ions at lower concentrations. The order of adsorption of metals on bentonite at 20 °C is Zn(II) > Cu(II) > Co(II) at pH 3.0, 5.0 and 7.0; Zn(II) > Co(II) > Cu(II) at pH 9.0 according to Langmuir and Freundlich isotherm data. The adsorption isotherms are obtained and they are well described by the Langmuir and Freundlich equation. The adsorption capacity depends on the initial metal concentration, initial pH and temperature. With increase in initial pH value, adsorption of heavy metals on bentonite increased while adsorption of heavy metals decreased with increase in medium temperature. Also, the distribution coefficient (K_{d}) decreased with increasing initial metal ion concentration. It increased with increase in pH value of the adsorbent mixture and sharply increased at pH 9.0. The sharp increase may be due to precipitation of metal ions as hydroxide salts or increase in the surface charge density of adsorbent with increasing pH value. The selectivity order of metal ions on bentonite has also changed in the order of Zn(II) > Cu(II) > Co(II). The DKR equation was also used to describe the adsorption isotherms of single-solute systems. The adsorption energy, E determined in the DKR equation (5.351 for Zn^{2+} ion and 9.709 for Zn^{2+}, 3.716 for Cu^{2+} on bentonite at pH 7.0 and pH 9.0, respectively) revealed the nature of the ion-exchange mechanism or complex formation on the adsorbent-adsorbate system. The values of the adsorption energy, E, obtained by DKR isotherms indicated that an ion-exchange mechanism was operative for zinc and copper ions at pH 7.0 and 9.0. In addition, the adsorption capacity at the DKR region found to be below that observed at the Langmuir region. These results show that bentonite can be used effectively for the removal of Zn^{2+} and Cu^{2+} ions based on ion-exchange mechanism from aqueous solution and wastewater. This naturally occurring clay mineral can provide a substitute for the use of expensive adsorption materials such as active carbon due to its availability and its relatively low cost. It was shown in many researches that activated carbon is an effective adsorbent for organic compounds, specifically for phenolic compounds. However, its high initial cost and the need for a costly regeneration system make it less economically viable as an adsorbent. Cost effectiveness, availability and adsorptive properties, are the main criteria for choosing an adsorbent to remove inorganic and organic compounds. Taking these criteria into consideration, it can be said that the naturally available bentonite will be able to use as a more economical adsorbent for the adsorption of the metal cations without requiring an expensive regeneration instead of active carbon being a conventional adsorbent.

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