



Effect of ionic strength on the adsorption of copper and chromium ions by vermiculite pure clay mineral

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ABSTRACT

It is important to assess the effects of ionic strength when studying adsorption of metal ions on clay mineral because the background salt may complex metals and compete for adsorption sites. The sorption behavior of vermiculite pure clay mineral has been studied with respect to copper and chromium as a function of ionic strength in single metal ion solutions. Background electrolytes used in these experiments were KCl, NaCl and NH_4Cl . The studies were conducted by a batch method at temperature 25°C . The adsorption capacity and adsorption energy for each metal ion were calculated from the Langmuir adsorption isotherm.

Also the competitive adsorption behavior of some heavy metal ions such as Cr(III), Cu(II), Ni(II) and Co(II) by vermiculite pure clay mineral was studied. The result shows the competition between coexisting heavy metal cations for the same adsorption sites of an adsorbent. However, when trivalent metal was added to the solution it competitively replaced divalent ions that had been previously adsorbed onto the vermiculite pure clay mineral, resulting in the desorption of these metals into the solution.

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1. Introduction

Environmental pollution, as a consequence of the industrialization process, is one of the major problems that have to be solved and controlled. Heavy metals are not biodegradable and have become an ecotoxicological hazard of prime interest and increasing significance owing to their harmful effect on human physiology and other biological systems when they exceed the tolerance levels. Copper has been reported as one of the most widely used heavy metal in electrical and electroplating industries. Since copper is an essential metal in a number of enzymes for all forms of life, problems arise when it is deficient or in excess. Excess copper accumulates in the liver, brain, skin, pancreas and myocardium. The removal of Cr(III) from contaminated wastewater is necessary because of its high toxicity to living organisms. It is both a mutagen and carcinogen at low sub-ppm levels. It is highly soluble in aquatic environment and can be readily adsorbed by living organisms. Once it accumulates in living organisms beyond the allowable concentration, it can cause severe health problems [1,2]

A number of technologies for the removal of heavy metal ions from aqueous solutions have been developed over the years [3]. The most important of these techniques include chemical precipitation, filtration and reverse osmosis. However, all these techniques have

their inherent advantages and limitations in application. The process of adsorption has become one of the preferred methods for removal of toxic contaminants from water as it has been found to be very effective, economical, versatile and simple [4]. Adsorption has the additional advantages of applicability at very low concentrations, suitability for using batch and continuous processes, ease of operation, little sludge generation, possibility of regeneration and reuse, and low capital cost [5]. The processes have acquired global importance for minimization of the problem of contamination of water and air, and these processes have become a significant addition to green chemistry endeavours.

The main properties of the adsorbents are strong affinity and high loading capacity for the removal of heavy metals. Natural adsorbents have generally these properties. Ion-exchange and adsorption mechanisms of clay minerals have been used to remove different heavy metals from aqueous solution [6–10].

Clays play an important role in the environment by acting as a natural scavenger of pollutants by taking up cations and anions either through ion exchange or adsorption or both. Thus, clays invariably contain exchangeable cations and anions held to the surface. The prominent cations and anions found on clay surface are Ca^{2+} , Mg^{2+} , H^+ , K^+ , NH_4^+ , Na^+ , and SO_4^{2-} , Cl^- , PO_4^{3-} , NO_3^- . These ions can be exchanged with other ions relatively easily without affecting the clay mineral structure. Large specific surface area, chemical and mechanical stability, layered structure, high cation-exchange capacity (CEC), etc., have made the clays excellent adsorbent materials. Both Brönsted and Lewis type of acidities in

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clays have boosted the adsorption capacity of clay minerals to a great extent. The Brønsted acidity arises from hydrogen ions on the surface [11–13].

This work is focused on the investigation of the effect of KCl, NaCl and NH₄Cl on copper and chromium ions adsorption into vermiculite pure clay mineral in single metal solutions at 25 °C. The adsorption isotherms for Cu(II) and Cr(III) from their aqueous solutions were investigated to explore the possible mechanism of the metal binding to adsorbent. Competitive adsorption onto the clay was also investigated in solutions containing binary mixtures of heavy metals.

2. Materials and methods

2.1. Materials

All chemicals used were of analytical reagent grade. Aqueous metal solutions were prepared by dissolving appropriate quantities of reagent grade metal chloride salts (Aldrich Chemical Company, USA). Doubly distilled water was used throughout. The adsorption behavior was studied at the solution pH and agitated for a 24-h period.

The vermiculite sample used was supplied by the North Transvaal, Africa Rochester N.I. The elemental composition of the clay sample was determined by thermo Jarrell Ash atomic absorption spectrophotometer after solubilisation by acid digestion in microwave oven. The chemical compositions of vermiculite sample in weight percentage are: SiO₂ (44.62), Al₂O₃ (9.18), Fe₂O₃ (5.46), CaO (0.78), MgO (20.44), Na₂O (0.11), K₂O (0.48) and fire loss (18.93). The cation-exchange capacity of vermiculite samples was 94 meq./100 g determined by the ammonium acetate method [14].

2.2. Instruments

Thermo Jarrell Ash atomic absorption spectrophotometer (AAS) model (POEMS III) USA was used to analyze the elemental composition of the clay. A Milestone MLS Mega microwave laboratory unit was used for the dissolution of the clay. UV–vis Perkin Elmer-lambda spectrophotometer model 201, pH meter model OP-02/2 (Germany) with a combined electrode reading to ±0.05 pH value and water bath with thermostat and 100 mL double jacket cell (UKT-Germany) were used.

2.3. Adsorption studies

2.3.1. Batch equilibrium

A known amount of adsorbent was shaken together with 40 mL of an aqueous metal solution in a 100-mL stopper bottle using a water bath maintained at constant temperature. From the preliminary experiments, it had been found that the equilibrium was reached within the period of for all cases. The batch study conditions for single metal ion are optimum adsorbent dosage, 1.25 g/L; different initial concentration of Cr(III) and Cu(II) solutions was prepared by proper dilution from stock 1000 mg/L Cr(III) and Cu(II) standard, shaking time, 24 h, temperature, 25 °C. At the end of time, the mixture was filtered and the metal ion's concentration in the filtrate was determined using UV–vis spectrophotometer. In order to determine the concentration of Cr(III) and Cu(II) ions in the unknown solutions we will first construct a standard plot of the concentration of Cr(III) and Cu(II) ions vs. the absorbance of solutions having known Cr(III) and Cu(II) ions concentrations. According to Beer's Law, absorbance is directly proportional to concentration and so the resulting plot should be a straight line. This graph will be used to determine the concentrations of the unknown Cr(III) and

Cu(II) ions. The amounts of the metal ions adsorbed were obtained by difference.

2.3.2. Effect of ionic strength on distribution coefficient

Useful information regarding salts effect was obtained by measuring distribution coefficient of copper and chromium ions on vermiculite pure clay mineral at 25 °C in the presence of various concentrations of different electrolyte solutions. Background electrolytes used in these experiments were 0.5, 1.0, 3.0 and 5.0% KCl, NaCl and NH₄Cl.

2.3.3. Competitive adsorption behaviors

In order to validate the competitive sorption between metals, solutions of heavy metals (Co, Ni, Cu and Cr as chloride; reagent grade; Aldrich) were prepared in distilled water without adjusting the pH. A metal solution containing a fixed concentration 200 mg/L was mixed with other solutions at various concentrations. Each solution mixture was shaken with 1.25 g/L adsorbent at 25 °C. The experimental set-up was equilibrated 24 h. At the end of time, the mixture was filtered and the metal ion concentration in the filtrate was determined using UV–vis spectrophotometer. The amounts of the metal ions adsorbed were obtained by difference. The concentration of metal in the aqueous solutions before and after adsorption was obtained using the standard curve.

2.3.4. Determination of distribution coefficient

Distribution coefficients were determined by a batch technique. Weighted amounts of adsorbent were placed in flasks, metal ion solutions were added with gentle stirring until equilibrium. The absorbance of metals in aqueous solutions was measured with UV–vis spectrophotometer at the wavelength corresponding to the maximum absorbance. Before each measurement, the baseline of the spectrophotometer was calibrated against the solvent. The standard curve was obtained by plotting absorbance versus concentration

The K_d value was computed from the following formula [15].

$$K_d = \frac{\text{Amount of metal ion on adsorbent}}{\text{Amount of metal ion in solution}} \times \frac{V}{m} \text{ (ml/g)} \quad (1)$$

$$K_d = \frac{(C_i - C_{eq})}{C_{eq}} \times \frac{V}{W} \text{ (ml/g)} \quad (2)$$

where C_i and C_{eq} is the initial and final (equilibrium) concentration of studied metal ions in their aqueous solutions at the beginning and at the end of removal experiments respectively, V is the volume of the solution in mL and, m is the mass of adsorbent in g.

3. Results and discussion

3.1. The effect of ionic strength

Vermiculite is typical clay and consists of tetrahedral–octahedral–tetrahedral sheets. The two tetrahedral silicate layers are bonded together by one octahedral magnesium hydroxide-like layer and the structure is often referred to as 2:1 phyllosilicate. When tetravalent silicon is substituted by trivalent aluminum in the tetrahedral layer of the vermiculite sheet, a negative charge is generated on the layer and, thus, hydrated magnesium is adsorbed on the tetrahedral layer between the sheets to maintain electro neutrality. These magnesium ions can be easily cation exchanged with other cationic species such as copper, which partly contribute to the high cation-exchange capacity of vermiculite [16].

Vermiculite can adsorb heavy metals via two different mechanisms: (1) through cation exchange at the planar sites, resulting from the interactions between metal ions and negative permanent charge (outer-sphere complexes) and (2) through the formation of

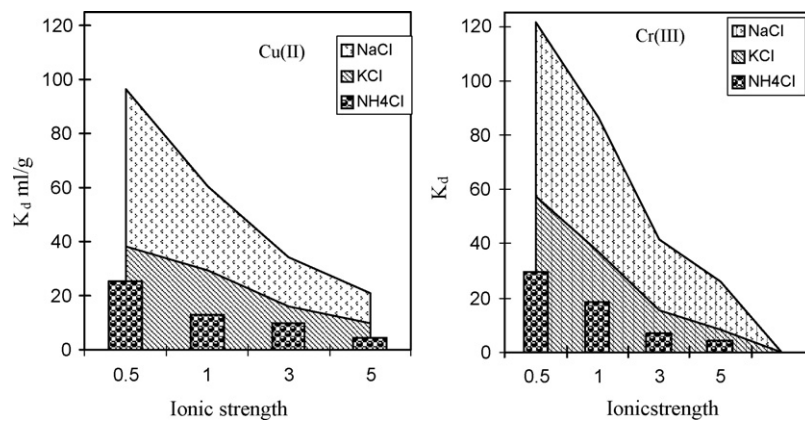


Fig. 1. The distribution coefficient, K_d of metal ions by vermiculite pure clay mineral as a function of ionic strength (adsorbent dosage, 1.25 g/L; Cr(III) and Cu(II) concentration, 200 mg/L shaking time, 24 h, temperature, 25 °C).

inner-sphere complexes through Si–O– and Al–O– groups at the clay particle edges. Both mechanisms are pH dependent but the latter is particularly influenced by pH because in acid conditions $\text{pH} < 4$ most silanol and aluminol groups on edges are protonated [17,18].

The effect of ionic strength on the sorption of some metal ions onto vermiculite pure clay mineral was studied. The sorption experiment was conducted by equilibrating 1.25 g/L sorbent with 200 mg/L of Cr(III) or Cu(II). Background electrolytes used in these experiments were 0.5, 1.0, 3.0 and 5.0% KCl, NaCl and NH_4Cl at 25 °C. Fig. 1 shows that the distribution coefficients, K_d decreased with increase in ionic strength of the salt solutions for the two metal ions under studied. The decrease in distribution coefficients, K_d with increase in ionic strength is primarily attributed to the affinity between metal ions and Cl^- ions. The low distribution coefficients, K_d of metal ions at high concentration of Cl^- in the solution is due to the formation of metal chloride. That is, the amount of free metal ions remaining in solution for sorption is reduced considerably and hence the low sorption of metal ions. The relatively large change in the, K_d values, for metal ions at lower ionic strength is due to ion-exchange effects. Increasing ionic strength will increase the ratio of chelation to ion exchange and at very high salt concentration; ion exchange will become very small. A further increase in the salt concentration may significantly lead to a decrease in the distribution coefficients [19]. A corresponding decrease in metal ions distribution coefficients with increasing ionic strength can be attributed to (1) increasing K^+ or Na^+ and NH_4^+ concentration with increasing ionic strength and therefore increasing competition for the sorption sites on each sorbent and, (2) decreasing activity of metal ions in solution due to increasing non-ideality of solution with ionic strength. This non-ideality is due to increasing electrostatic interaction and results in the formation of ion pair. Many researchers [20–22] showed that at low ionic strength heavy metal sorption on clay minerals takes place onto both planar and edge sites, but

an increase in ionic strength supplies more positive ions which compete with the heavy metals for the sorption sites on the clay, especially for the planar sites which are considered of lower affinity. Therefore, at 0.5% ionic strength the sorption of heavy metals will mostly occur on the high affinity edge sites.

The salt cation had large effect on each metal ion's sorption. For the three salt cations, the greatest metal ions sorption was in the Na^+ background, followed by K^+ and NH_4^+ backgrounds. This could be due to the less competitive nature of Na^+ with each metal ion for sorption sites as compared to K^+ and NH_4^+ . The NH_4^+ was thought to resemble K^+ in cation-exchange reactions due to their similar ionic size and charge. The Na^+ , because of its large hydrated ionic size, forms only outer-sphere complexes with clay mineral, vermiculite surfaces, whereas K^+ and possibly NH_4^+ are able to form inner-sphere complexes. The inhibitory effect of K^+ on metal ion's sorption as compared with Na^+ has been previously reported for acid sandy soils [23,24].

3.2. Adsorption isotherm

The equilibrium sorption isotherm is fundamentally important in the design of sorption systems. Equilibrium studies in sorption give the capacity of the sorbent. It is described by sorption isotherm characterized by certain constants whose values express the surface properties and affinity of the sorbent. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and that remaining in solution at fixed temperature at equilibrium. The most common shape of the graph of amount adsorbed for unit weight of adsorbent versus the concentration in the fluid in equilibrium is Langmuir sorption isotherm. The Langmuir sorption isotherm has been successfully applied to many pollutants sorption processes and has been the most widely used sorption isotherm for the sorption of a solute from a liquid solution. A basic assumption of the Lang-

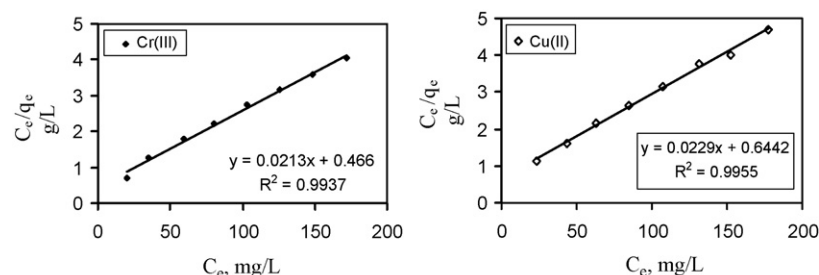


Fig. 2. Langmuir isotherms of Cr(III) and Cu(II) ions adsorption by vermiculite pure clay mineral (adsorbent dosage, 1.25 g/L; shaking time, 24 h, temperature, 25 °C).

Table 1

Langmuir isotherms constants for Cr(III) and Cu(II) ions adsorbed on vermiculite pure clay mineral (adsorbent dosage, 1.25 g/L; shaking time, 24 h, temperature, 25 °C).

Langmuir constants	Cr(III)	Cu(II)
q_m , mg/g	46.948	43.668
K_a , L/mg	0.046	0.036
R^2	0.994	0.996

muir theory is that sorption takes place at specific homogenous sites within the sorbent. It is then assumed that once a metal ion occupies a site, no further sorption can take place at that site. The rate of sorption to the surface should be proportional to a driving force which times an area. The linear form of Langmuir isotherm [25] is given by:

$$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{1}{q_m} C_e$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of metal ion sorbed (mg/g), and q_m is q_e for a complete monolayer (mg/g) and K_a is sorption equilibrium constant (L/mg). q_m and K_a are Langmuir constants related to sorption capacity and energy of sorption, respectively. To get the equilibrium data, initial metal ion's concentration were varied while the adsorbent mass in each sample was kept constant, 24 h of equilibrium periods for sorption experiments were used to ensure equilibrium conditions. The equilibrium data for metal cations over the concentration range from 50 to 275 mg/L at 25 °C were investigated. Fig. 2 shows the linear plot of C_e/q_e versus C_e that gives a straight line of slope $1/q_m$ and intercept $1/K_a q_m$. The values of the Langmuir constants q_m and K_a have calculated and presented in Table 1 for the sorption of Cr(III) and Cu(II) onto vermiculite pure clay mineral. The coefficient of determination indicates that there is a strong positive relationship for the data and that the metal cation-exchange sorption follows the Langmuir sorption isotherm. The sorption capacity, q_m , which is a measure of the maximum sorption capacity corresponding to complete monolayer coverage showed that the vermiculite pure clay mineral had a mass capacity for Cr(III) (46.948 mg/g) larger than Cu(II) (43.668 mg/g). The data in Table 1 further indicated that, the effectiveness of vermiculite pure clay mineral in the sorption of two metals from aqueous system was Cr(III) > Cu(II). This preferential sorption behavior could be explained in terms of ionic radii of the metal ions (Cr(III) = 0.69 Å and Cu(II) 0.71 Å). The element with smaller ionic radius will compete faster for exchange sites than those of larger ionic radius. The larger the charge of an ion, the smaller, the ionic radius, hence the charge of an ion may influence its ability to sorb on sorbents. Hydration energy is an important factor in sorption process accounting for the hydrolysis of metal ions, which occurs by the replacement of water liquids in the inner coordination sphere with hydroxo groups. Adsorption may be related to the loss of the entire hydration sphere that precedes hydrolysis [26]. The observed order indicates that Cr(III) may have greater accessibility to the surface of certain pores than Cu(II) due to its small ionic radius.

The Langmuir constant values (q_m) can be used to estimate the specific surface area, S , of sorbent [25] using the following equation

$$S = \frac{q_m N A}{M} \quad (3)$$

where S is the specific surface area, m^2/g of adsorbent; q_m is monolayer sorption capacity, gram metal per gram adsorbent; N is Avogadro number, 6.02×10^{23} ; A is the cross sectional area of metal ions, M is molecular weight of metal. The cross sectional areas of Cr(III) and Cu(II), have been determined to be 1.49 \AA^2 and 1.58 \AA^2 respectively. The maximum specific surface area of vermiculite pure clay mineral towards Cr(III) and Cu(II) binding are $8.257 \text{ m}^2/g$ and $6.168 \text{ m}^2/g$ respectively. The increased adsorbent surface area

Table 2

The dimensionless separation factor K_R for Cr(III) and Cu(II) ions adsorbed by vermiculite pure clay mineral (adsorbent dosage, 1.25 g/L; shaking time, 24 h, temperature, 25 °C).

Initial metal ion's concentration, mg/L	K_R	
	Cr(III)	Cu(II)
50	0.303	0.357
75	0.225	0.270
100	0.179	0.217
125	0.148	0.182
150	0.127	0.156
175	0.111	0.137
200	0.098	0.122
225	0.088	0.110
250	0.080	0.100
275	0.073	0.092

tends to increase the adsorbent removal efficiency [27]. The result indicates that vermiculite pure clay mineral preferentially sorbed Cr(III), followed by Cu(II).

To confirm the favorability of the adsorption process, the separation factor (K_R) has been calculated. The variation of the separation factor (K_R) with the initial concentration of the solution (C_0 , mg/L) is presented in Table 2. The K_R values range from 0.092 to 0.303 between 50 and 275 mg/L and approaches zero with increase in the C_0 value. This parameter was found to be between 0 and 1 and confirm that the ongoing adsorption process is favorable.

3.3. Competitive adsorption behavior

Pollutants can generate multi-component solutions, and the competition among the heavy metals onto the adsorbent can affect the mobility of heavy metals and the efficiency with which they can be removed from such multi-component solutions. Distribution coefficients (K_d) represent the sorption affinity of the Cr(III), Cu(II), Ni(II) and Co(II) in solution for the vermiculite and can be used as a valuable tool to study metal cation mobility and retention in vermiculite. A high values of K_d indicate that the metal has been retained by the solid phase through sorption reactions while low values of K_d indicate that a large fraction of the metal remains in solution [28].

The objective of this part work was to study the effect of two metal ions coexistence on the total adsorptive of vermiculite pure

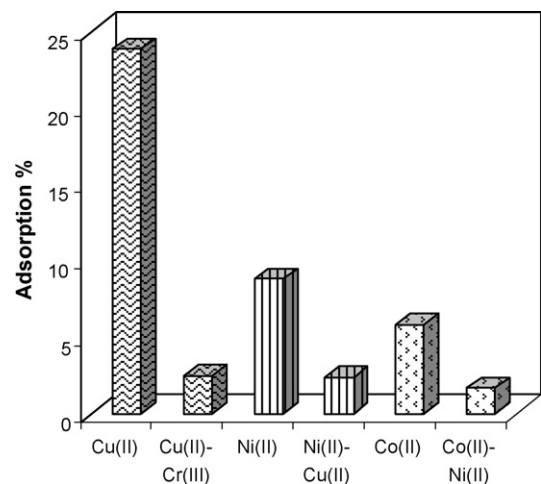


Fig. 3. The effect of two metal ions coexistence on the adsorption by vermiculite pure clay mineral. (The concentration of ions in each binary mixture are constant) [Cu(II)] = [Ni(II)] = [Co(II)] = [Cr(III)] = 200 mg/L, concentration of single ions = 200 mg/L (adsorbent dosage, 1.25 g/L; shaking time, 24 h, temperature, 25 °C).

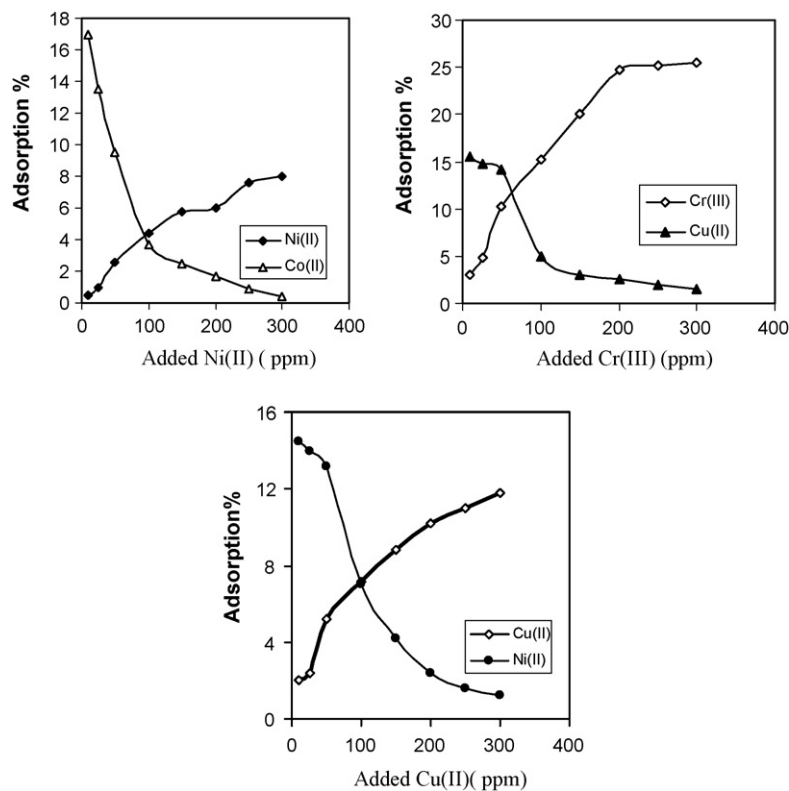


Fig. 4. The effect of added Ni(II), Cr(III) and Cu(II) ions in different concentrations on the adsorption by of vermiculite pure clay mineral at constant concentration of [Co(II)] = [Cu(II)] = [Ni(II)] = 200 mg/L (adsorbent dosage, 1.25 g/L; shaking time, 24 h, temperature, 25 °C).

clay mineral. The experiment was carried out keeping the total concentration changeless and changed each metal ion concentration. The competitive adsorption of Co(II)–Ni(II), Cu(II)–Cr(III) and Ni(II)–Cu(II) binary mixtures were investigated. The initial metal ion concentration was equal 200 mg/L for each metal ion. 1.25 g/L of the vermiculite pure clay mineral was added to each binary solution. The adsorption behavior was studied at the solution pH and agitated for a 24-h period.

The study of a synthetic Co(II)–Ni(II) solution indicated the presence of adsorption competition between two metals. As shown in Fig. 3, values of Co(II) adsorption obtained from the experiment results intended for the binary mixture were less than those for the single component solution. The similar adsorption behavior of these metals onto the clay is likely due to their similar physicochemical properties, such as electronegativity, ionic radius, and electronic charge [29]. This result indicated that Co(II) and Ni(II) ions competed with each other for the same sites on the vermiculite pure clay mineral. The same result was observed in each, Cu(II)–Cr(III) and Ni(II)–Cu(II) binary mixture. However, when Cr(III) or Cu(II) was added to the solution it competitively replaced Cu(II) and Ni(II) ions respectively which had been previously adsorbed onto the vermiculite pure clay mineral, resulting in the desorption of these metals into the solution.

In order to confirm competitive adsorption interactions between heavy metals, batch experiments were conducted in which varying concentrations of a metal ranging from 10 to 300 mg/L added to vermiculite pure clay mineral that already possessed an adsorbed metal (Fig. 4). The results of these experiments show that in Cu(II)–Cr(III) binary mixture the amount of Cr(III) adsorbed by vermiculite pure clay mineral increased in proportion to the increase in concentration of the tested solution, while Cu(II) showed a corresponding displacement from the clay surface into the surrounding solution. In Ni(II)–Cu(II) binary mixture, the amount of Cu(II) adsorbed by vermiculite pure clay mineral increased in pro-

portion to the increase in concentration of the tested solution, while Ni(II) showed a corresponding displacement from the clay surface into the surrounding solution. In Co(II)–Ni(II) binary mixture the amount of Ni(II) adsorbed by vermiculite pure clay mineral increased in proportion to the increase in concentration of the tested solution, while Co(II) showed a corresponding displacement from the clay surface into the surrounding solution.

This result shows that competition between coexisting heavy metal cations for the same adsorption sites of a clay clearly affects adsorption behavior in such a way that the pure clay mineral desorbed more Cu(II), Ni(II) and Co(II) for each binary mixture Cu(II)–Cr(III), Ni(II)–Cu(II) and Co(II)–Ni(II) respectively with increasing concentrations of added Cr(III), Cu(II) and Ni(II) respectively. In Cu(II)–Cr(III) binary mixture the results are likely due to a high adsorption affinity of Cr(III) onto clay that led to Cr(III) ions to replace the Cu(II) ions that had previously been adsorbed onto the adsorption sites of the vermiculite pure clay mineral. Since monovalent or bivalent ionic species are sorbed to a lesser extent than the other polyvalent ions, Cu(II) do not suppress the prevailing affinity of Cr(III) for the binding sites of adsorbent. It is well documented that ionic charges and ionic radii of cations affect ion exchange as well as adsorption [30,31]. The results indicate that it is important to understand the mechanisms of competitive adsorption of coexisting metals onto adsorbent for the effective operation of ion-exchange processes for the removal of heavy metals in wastewater or polluted water.

4. Conclusions

Metal adsorption is sensitive to changes in the concentration of electrolyte if electrostatic attraction is the significant mechanism for metal removal. However, an increased amount of electrolyte seemed to decrease the access of the metal ions to adsorbent surface

for metal binding. The equilibrium isotherm analysis of the experimental data showed that the adsorption of Cr(III) and Cu(II) ions onto the vermiculite pure clay mineral follows Langmuir isotherm. It was noted that ionic radius has an influence in the magnitude of metal loading on the adsorbent. The result indicates that vermiculite pure clay mineral preferentially sorbed Cr(III), followed by Cu(II).

The presence of a single heavy metal in natural water and wastewater is a rare situation. Therefore, it is essential to fully understand the mechanism of competitive adsorption of coexisting metals onto the clay mineral for effective operation of ion-exchange process. The sorption properties of heavy metals onto vermiculite pure clay mineral were strongly influenced by the presence of competing cations in the solution. Values of adsorption obtained from the experiment results for the binary mixture were less than those for the single component solution. In a binary mixture, trivalent metal replaced the adsorbed divalent metals that had previously been adsorbed onto the adsorption sites of the vermiculite pure clay mineral.

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