

Adsorption of zinc from aqueous solutions to bentonite

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Abstract

The adsorptive properties of natural and Na-enriched bentonite in zinc rich aqueous environment have been studied. The results show that adsorption behavior of both bentonites was strongly depending on the pH. At low pH values, the mechanisms that govern the adsorption behavior of bentonites are dissolution of crystal structure and competition of the metal ions with the H⁺. Between pH 4 and 7, the basic mechanism is an ion exchange process. The alkaline and alkaline earth metals located in the exchangeable sites of bentonites are replaced with Zn²⁺ cations present in the aqueous solution. At higher pH values (i.e. pH 8), formation of zinc hydroxyl species may result either participation to the adsorption or precipitation onto the bentonites. Therefore, a rapid increase in the equilibrium removal of zinc was obtained above pH 7. Increase in the initial metal ion concentration led to the increase in equilibrium adsorption to a certain degree; then, a plateau was obtained at higher concentrations. The rate of zinc removal depends also on the solid concentration of the suspension. Reducing the slurry concentration allows particles to get in the more dispersed form, resulting higher available sorption sites for zinc. As a result, the adsorption performance of Na-enriched bentonite is better than the natural bentonite in all physical and chemical changes. The data were fitted both Langmuir and Freundlich isotherms.

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1. Introduction

Releasing industrial wastewaters and flooding of ore mines into the environment results in contamination of soils and groundwater. Moreover, many inorganic and organic substances that may cause health problems can be detected in agricultural products as a result of contamination transport and pesticide usage. The remediation technologies used for clean up processes of polluted areas are time consuming and expensive. Despite their high cost, clay-based barriers are built up at the waste disposal areas to protect the migration of hazardous contaminants through the environment. Hence, plumes generated by the leachates are capped and immobilized into a clay liner.

The natural materials widely used in liner applications are (i) clays and (ii) bentonite/sand mixtures. The suitable compaction of liner material reduces the permeability and strengthens the barrier system. The utilization of clays as a liner material has been applied for the last few decades [1–4]. In addition, Kleppe and Olson [5] and Kenney et al. [6] proposed the bentonite/sand mixture as an alternative material to the clay liners. Recent studies showed that bentonite/zeolite mixtures could be used in a barrier system as well [7,8].

On account of higher surface area and cation exchange capacity, bentonite (mainly montmorillonite) is the most preferable clay mineral for barrier applications. Bentonite is a 2:1 mineral with one octahedral sheet and two silica sheets, which forms a layer. Layers are held together by van der Waals forces. Because of these weak forces and some charge deficiencies in the structure, water can easily penetrate between layers and cations balance the deficiencies [9].

Since it is an important constituent in a barrier system, the physical and chemical performance of bentonite should

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Table 1
Mineralogical compositions of bentonites with their specific surface area and cation exchange capacity values

Materials	SSA (EGME) (m ² /g)	CEC (meq/100 g)	Mineralogical compositions
Natural bentonite	393.44	132.33	Montmorillonite, illite, feldspar, quartz
Na-enriched bentonite	441.96	67.11	Montmorillonite, illite, carbonate, feldspar, kaolinite

be known before using it as a liner material. For evaluating its behavior against chemical attack, bentonite attracted the researcher's concern for a long time and has been studied extensively. Most of these studies considered the adsorption characteristics of bentonite for some toxic elements. It is well documented that bentonite is an efficient adsorbent for some heavy metals, especially for lead [10,11], copper [12], cadmium [10,12,13] and zinc [14]. In addition to bentonite's great tendency for adsorbing heavy metals, it is also effective for adsorbing the phenols and related compounds from the wastewaters [15–17].

Detailed adsorption studies for bentonite were given in the literature for some heavy metals, i.e. lead, copper and nickel [10–13]. However, studies of its behavior in the presence of zinc ions under different pH conditions, slurry and heavy metal concentrations are very scarce. The main purpose of this study is to fill the gap for zinc uptake for bentonite under different physical and chemical conditions. For this reason, a detailed study was conducted in order to determine the influence of initial pH, initial metal ion concentration and slurry concentration on adsorption characteristics of natural and Na-enriched bentonites. Langmuir and Freundlich isotherms were also compared with the experimental data.

2. Materials and methods

2.1. Materials

The natural and commercially available Na-enriched bentonites were obtained from Süd-Chemie Co., Balıkesir, Turkey. Bentonites were in the clod sized forms when first received. Later, they were powdered in a mortar and sieved from no. 200 (75 μm) sieve to obtain finer grains. Powdered bentonites were dried for 1 week in an oven at 60 °C before the experiments. The mineralogical and chemical compositions of the materials were determined by X-ray diffractometer (XRD) and inductively coupled plasma (ICP). The cation exchange capacity and specific surface area were obtained by the Na-method [18] and ethylene glycol monoethyl ether (EGME) method [19]. The results of the mineralogical and chemical compositions of the bentonites are presented in Tables 1 and 2, respectively.

Table 2
Chemical compositions of materials

Materials	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MgO (%)	CaO (%)	Na ₂ O (%)	K ₂ O (%)
Natural bentonite	54.30	19.54	1.25	4.13	2.09	0.13	0.73
Na-enriched bentonite	47.28	10.97	1.28	6.81	7.90	2.81	0.22

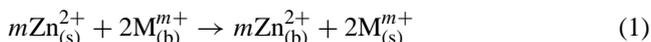
2.2. Methods

Puls and Bohn [20] stated that zinc adsorption onto the calcium saturated bentonite was higher for Cl⁻ solution than that of ClO₄⁻ and SO₄²⁻ because the formation of limited zinc–chloro complexes were due to the incompatibility of the harder Zn²⁺ with the soft Cl⁻. Therefore, ZnCl₂ solution was used in the batch experiments. A volume of 100 cm³ of zinc solutions with various amounts of bentonites was placed in an Erlenmeyer flask to commence the experiments. The initial metal ion concentration used in the tests ranged between 12.5 and 200 mg/l for both clays. Since it was intended to obtain the slurry concentrations in the range of 1.0–10.0 g/l, bentonites were weighed between 0.1 and 1 g. The batch adsorption experiments were also conducted at different pH levels (i.e. pH 3–8) and solution pHs were adjusted by adding diluted NaOH and HCl solutions. NaOH and HCl were prepared in 0.01N stock solutions and diluted with water in another flask and then, added to the solutions to arrange the pH. The pHs of the solutions were adjusted before adding the bentonites. This is because bentonite had a tendency to increase the solution pH after adding into the solution. The agitation speed was constant and fit 100 rpm during the test. The experiments were terminated at a contact time of 2 days. Most of the zinc ions were adsorbed by the bentonites in the first 6 h. After centrifugation, the supernatant liquid was used in UNICAM atomic adsorption spectrophotometry in order to determine the equilibrium zinc concentration in the solution.

3. Results and discussions

3.1. Determining the amount of adsorbed zinc ions, q_e

The interaction between the zinc ion and bentonite can be given by the equilibrium:



where m is the exchangeable cation valence M (Na, K, Ca, Mg) and subscripts (s) and (b) denote solution and bentonite phases, respectively.

The amount of adsorbed zinc ions by any material can be given by:

$$q_e = \frac{C_i - C_e}{S} \quad (2)$$

where q_e , C_i , C_e and S are the adsorbed metal ions onto the bentonites (mg/g), initial metal ion concentration (mg/l), equilibrium metal ion concentration (mg/l) and slurry concentration (g/l), respectively.

The change in adsorption characteristics of bentonites against zinc ions during the testing period can be seen in Fig. 1. Fig. 1 indicates that zinc ions were adsorbed onto the natural bentonite within a few minutes; whereas Na-enriched bentonite reached equilibrium almost at the end of 25 h. This may be due to the limited replacement of alkaline and alkaline earth metals with zinc ions for natural bentonite. On account of higher ionic radius of Na^+ , sodium treated bentonite has more expanded sheets between the layers than the natural bentonite. The adsorption may take place on the outer surface and in the interlayers of the bentonites. The gradual increase in the zinc uptake by Na-enriched bentonite pointed out the continuity of the replacement of zinc with sodium during 24 h; then, it became constant at the end of another 24 h. For the first 4 h, Na-enriched bentonite followed a lateral path within a few minutes like natural bentonite. Then, a gradual increase was observed from 4 to 24 h that may be attributed to the interlayer exchange of the diffused zinc and sodium ions held on the inner surface layers. Therefore, zinc uptake at the beginning is about 1.5 times higher for Na-enriched bentonite than the natural bentonite. However, adsorption ability for Na-enriched bentonite reached three times higher value than that of natural bentonite at the end of the experiments. Triantafyllou et al. [21] stated that the time required to reach steady state of adsorption differs with the sample characteristics, metal ion and pH. Thus, we deter-

mined the factors affecting the adsorption characteristics of natural and commercially Na-enriched bentonites.

3.2. Influence of solution pH

To determine the pH effect on adsorption capacity of materials, solutions were prepared at different pH levels from 3 to 8 before adding bentonites. Fig. 2 shows the change in zinc uptake by both bentonites at different initial pH levels. As can be seen from figure, adsorption capacity of Na-enriched bentonite increased when the initial pH of the solution was increased from 3 to 4. Although the increased adsorption capacity in this region is very pronounced for the Na-enriched bentonite, such increment is not observed for natural bentonite. From pH 4 to 7, a plateau was noted and there was negligible difference in the sorption of Zn^{2+} onto the bentonites within this range. Then, adsorption of Zn^{2+} by both bentonites suddenly increased to 90 mg/g when the initial pH of the solution was 8.

These results are in agreement with other studies performed with montmorillonite [22–24]. The mechanisms that influence the adsorption characteristics of bentonites can be given by dissolution, ion exchange/adsorption, and precipitation [22,23]. From Fig. 2, the lowest Zn^{2+} sorption rates were obtained at pH 3. This could be due to the increase in competition for adsorption sites by H^+ [22,24] and dissolution of Al^{3+} ions from the aluminosilicate layers [22]. Altin et al. [22] revealed that the removal efficiency of Pb^{2+} by montmorillonite decreased at low pH values (pH 2–4). The similar results were obtained by other researchers for some heavy metals such as Zn, Cd, Cu, Ni and Cr at pH 3 [24].

The basic mechanism that governs the adsorption characteristics of bentonites at pH ranging between 4 and 7 is adsorption and ion exchange. At these pH levels, exchangeable cations present at the exchangeable sites, i.e.

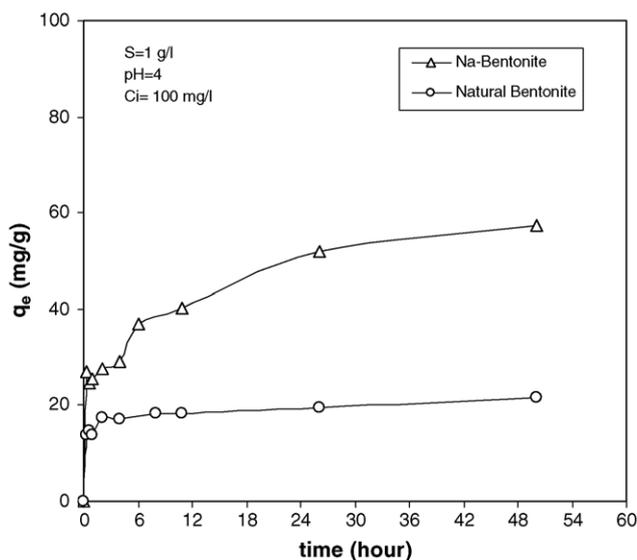


Fig. 1. Adsorption characteristics of materials during 2 days.

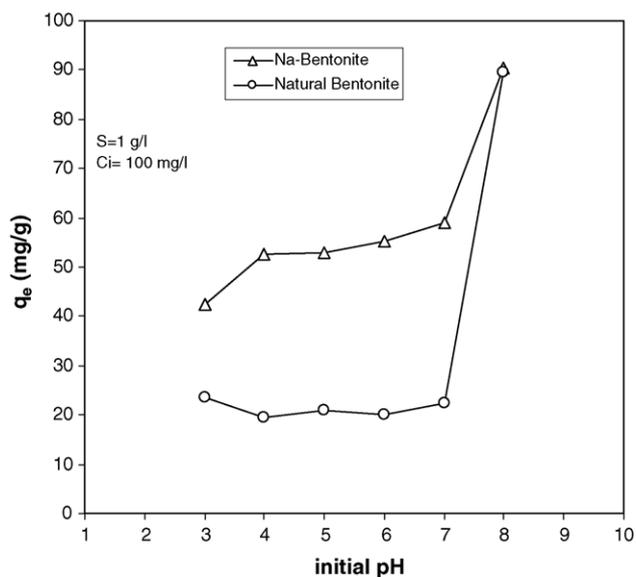


Fig. 2. Changes in the equilibrium removal of Zn^{2+} between pH 3 and 8.

Na^+ , K^+ , Ca^{2+} and Mg^{2+} are exchanged for Zn^{2+} cations in the aqueous solutions. Sharp increase was observed for both bentonites at high pH level (i.e. pH 8), which was due to the formation of zinc hydroxyl species. Depending on the pH and metal concentration, zinc may form complexes with OH^- , for example, $\text{Zn}(\text{OH})_2$, $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$, at higher pHs and as a result, zinc hydroxyl species may participate in the adsorption and precipitate onto the bentonite structure [14]. Previous studies showed a similar behavior for other heavy metals. For example, Barbier et al. [10] reported that lead sorption suddenly increased between pH 5.5 and 6.5 for montmorillonite and pH 6 and 7 for commercial bentonite; whereas cadmium sorption increased abruptly between pH 7 and 8 for both clays.

Measuring the final pHs of the suspension after a contact time of 50 h can give good information for revealing the above comments. Fig. 3 shows the final pH values at the end of the experiments.

Treating the Na-enriched bentonite at different initial pHs place the final pH value around 7 until pH 7 (dotted lines with arrowed tips); then, a sudden increase noted at pH 8. Unlike for Na-enriched bentonite, initial pH of the natural bentonite did not change significantly when the initial pH of the solution was 3. The rest of the changes in the initial solution pH were almost the same and were similar to the Na-enriched bentonite. As can be seen from this figure, increase in the final suspension pH may be attributed to the replacement of alkaline and alkaline earth metals (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) located in the exchange sites of bentonite with zinc ions existed in the solutions. Furthermore, carbonate, presented in the Na-enriched bentonite structure, may also be dissolved.

3.3. Influence of initial metal ion concentration

For the rest part of the experiments, pH 4 was used in order to evaluate the effect of initial metal ion concentration

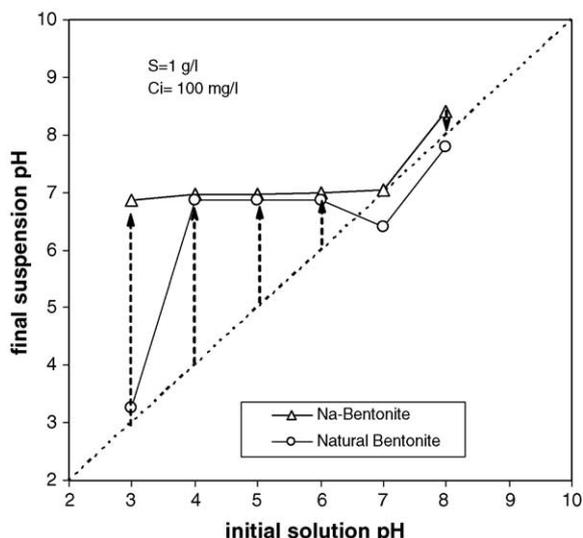


Fig. 3. Change in initial solution pH after the experiments.

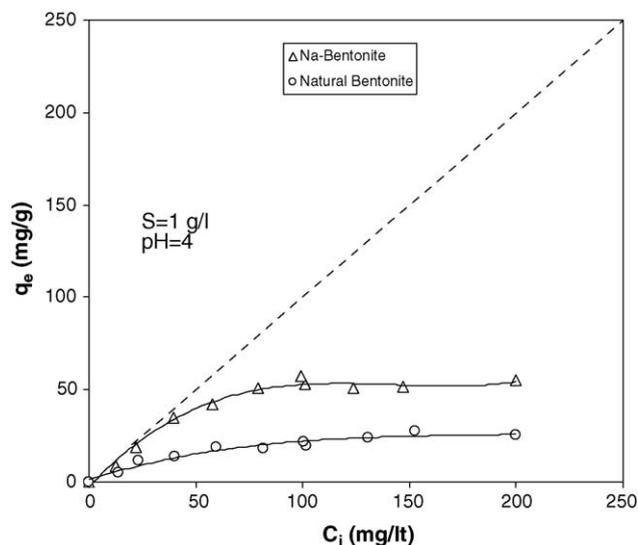


Fig. 4. Relationship between initial metal ion concentration and Zn^{2+} adsorption.

on adsorption characteristics of bentonites. Fig. 4 represents the change in adsorption behavior of both materials under different metal ion concentrations. As can be seen from Fig. 4, increasing the metal ion concentration leads to increase the Zn^{2+} uptake onto the materials to a certain point; then, a plateau occurs for both clays that indicate unavailability of adsorption sites on the bentonites for adsorption of zinc. The maximum adsorption capacity of Na-enriched bentonite and natural bentonite was obtained 54 and 24 mg/g, respectively.

The difference in the zinc sorption onto the bentonites may be due to the difference in the mineralogical compositions and associated cations in the exchangeable sites [25,26]. The lower selectivity of Zn^{2+} rather than other heavy metals such as Pb^{2+} , Cd^{2+} , Cu^{2+} by bentonites were given by some researchers [24,26,27]. Sheta et al. [26] investigated the sorption characteristics of natural zeolite and bentonite via zinc and iron and concluded that heavy metal uptake strongly depends on the mineralogical compositions of materials and kinds of heavy metal used in the tests. They found that one of two clinoptilolites had lower sorption ability for Zn^{2+} in comparison with the bentonite and other had higher ability than those of bentonite.

3.4. Influence of slurry concentration

Only limited data on the effect of slurry concentration on heavy metal removal by bentonites is available in the literature [11,21]. For assessment of the influence of slurry concentration, solutions were prepared in the range of 1.0–10.0 g materials/l. Initial metal ion concentrations were taken as 200 mg/l. Other situations such as pH and temperature kept constant. Fig. 5 expresses the effect of slurry concentration for Zn^{2+} removal from the aqueous solutions and the final pH of the suspension. Open and solid symbols denote the equilibrium removal and final suspension pH, respectively.

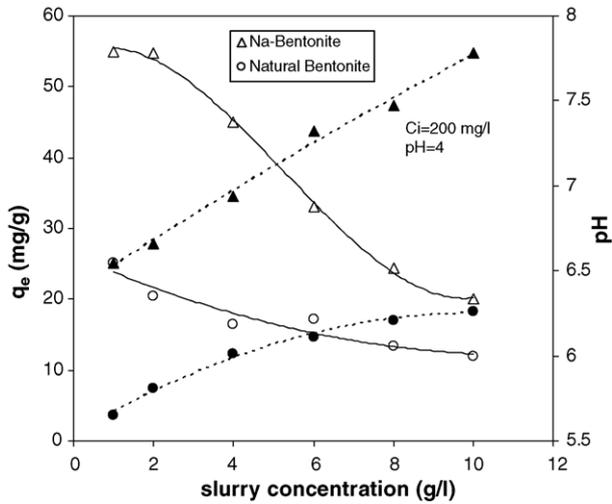


Fig. 5. Change in equilibrium removal of zinc under different bentonite contents and the path of final solution pH.

From Fig. 5, the amount of adsorbed zinc onto the natural bentonites and Na-enriched bentonite decreases with increasing the solids concentration. Raising the slurry concentration from 1 to 10 g/l reduces the zinc removal 64 and 52% for Na-enriched bentonite and natural bentonite, respectively. This may be due to the formation of aggregates as a result of flocculated particles for higher solid/liquid ratio. Diluting the suspension allows dispersing the particles, and therefore increases the available sorption sites between the particles [21,28].

The symmetrical change in final pH of the suspension with respect to slurry concentration can be seen in Fig. 5. For both materials, increase in the final pH can be attributed to the increase in the concentrations of alkaline ions released from bentonites.

3.5. Comparison of adsorption isotherms

Adsorption isotherms of bentonites for zinc ion were expressed mathematically in terms of the Langmuir and Freundlich models. The obtained experimental data are commonly well fitted with the Langmuir (Eq. (3)) and Freundlich (Eq. (4)) models:

$$q_e = \frac{K_L C_e}{1 + a C_e} \quad (3)$$

$$q_e = K_F C_e^n \quad (4)$$

If these equations are rearranged to the linear form; then,

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a}{K_L} C_e \quad (5)$$

$$\log q_e = \log K_F + n \log C_e \quad (6)$$

where K_L , a and K_F , n are the constants for Langmuir and Freundlich models, respectively. In addition to the experimental data, the linearized form of Langmuir and Freundlich

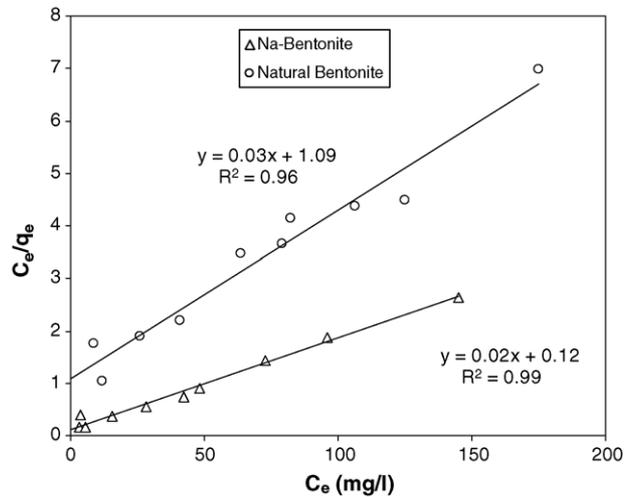


Fig. 6. Linearized Langmuir isotherms for Zn²⁺ removal by bentonites.

isotherms using Eqs. (5) and (6) for zinc ion removal by bentonites can be seen in Figs. 6 and 7, respectively.

As it is seen from Figs. 6 and 7, the experimental data for both clays are well fitted to the linearized Langmuir isotherm. Except for Na-enriched bentonite, linearized Freundlich isotherm corresponds to the experimental data as well. The values of K_L , a , K_F and n obtained from both models are presented in Table 3.

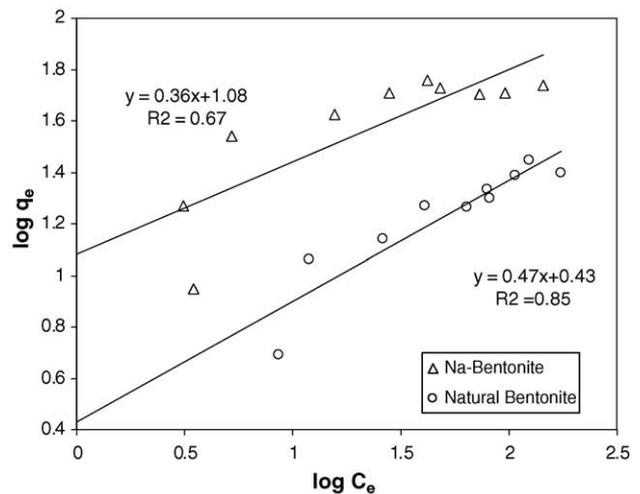


Fig. 7. Linearized Freundlich isotherms for Zn²⁺ removal by bentonites.

Table 3
The parameters for Langmuir and Freundlich isotherms

Isotherm parameters	Na-enriched bentonite	Natural bentonite
Langmuir		
K_L	8.271	0.921
a	0.144	0.03
Freundlich		
K_F	12.131	2.682
n	0.357	0.47

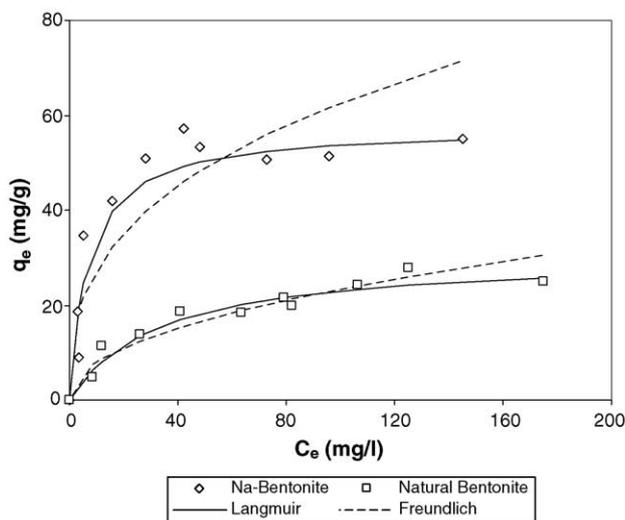


Fig. 8. Comparison of the experimental results with the q_e values obtained by Langmuir and Freundlich isotherms.

The comparison of the experimental values with the values of q_e obtained by both models is shown in Fig. 8. As it is seen from figure, Langmuir isotherms usually fitted better with the experimental data rather than Freundlich isotherms. Also, some other studies showed that Langmuir and Freundlich isotherms correspond well with the experimental results of some heavy metals [26].

4. Conclusions

The adsorption characteristics of natural bentonite and Na-enriched bentonite were determined for Zn^{2+} at different pH values, initial metal ion concentrations and slurry concentrations. The obtained results can be summarized:

- Results obtained from the effect of pH on the adsorption capacity of the bentonite indicated that the major factor which affected this parameter are competition of the H^+ ions with Zn^{2+} ions (under pH 4), ion exchange (pH 4–7), and participation of the heavy metal species to the adsorption and precipitation of some onto the bentonites (pH 8).
- Increase in the initial metal ion concentration leads to increase the adsorption to a degree; then, a plateau occurs, which indicates fully saturated materials with the heavy metal cations.
- Adsorption characteristics of all materials were influenced by the solid concentrations. Raising the slurry concentration lowers the uptake of Zn^{2+} from the solution. pH measurements showed symmetrical behavior with respect to the adsorption results that increase in the solid concentration led to increase the pH of the solution. This is because, the higher the solid concentration, the higher the replacement of alkaline and alkaline earth metals in the exchangeable sites with the zinc cations in the solution.

- The adsorption characteristics of Na-enriched bentonite are higher than the natural bentonite in all physical and chemical changes.
- The experimental results were well fitted with the Langmuir and Freundlich isotherms. The Langmuir isotherms correspond better with the experimental findings rather than Freundlich isotherms.

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