Adsorption of Cd$^{2+}$, Cu$^{2+}$, and Ni$^{2+}$ onto surfactant modified bentonite

Hajar Merrikhpour$^{a,*}$, Sara Mobarakpour$^{b}$, Seyedeh Bahareh Azimi$^{c}$

$^{a}$Department of Agriculture, Sayed Jamaleddin Asadabadi University, Asadabad 6541861841, Iran; emails: merrikhpour@sjau.ac.ir/hajar.merrikhpour@gmail.com
$^{b}$M.Sc. in Environmental Pollution, Islamic Azad University, Hamedan Branch, Iran, email: smobarakpoor@gmail.com
$^{c}$Research Group of Environmental Assessment and Risk, Research Center for Environment and Sustainable Development, RCESD, Department of Environment, Tehran, Islamic Republic of Iran, email: baharazimi94@gmail.com

Received 18 February 2022; Accepted 24 July 2022

Abstract

The content of heavy metals extremely exceeds from the international level due to the anthropogenic activities brought from point and nonpoint sources, soil and water contamination occurs and agricultural products become unhealthy for human consumption. This study aimed to apply modified bentonite for adsorption of cadmium (Cd$^{2+}$), copper (Cu$^{2+}$) and nickel (Ni$^{2+}$) from an aqueous phase. The natural Iranian bentonite was mixed with anionic surfactants, and sodium dodecyl sulfate (SDS) to produce modified bentonite. Batch experiments were performed in two individual and competitive solutions of Cd$^{2+}$, Cu$^{2+}$, and Ni$^{2+}$ (25–600 mg L$^{-1}$) in the present of Na-B and SDS (10, 20, and 40 Mm). The results demonstrated that SDS modified bentonite (SDS-B) treatments enhanced the sorption capacity of natural adsorbents with increasing pH. The SDS-B in 40 mM is of more adsorption efficiency to adsorb Cd$^{2+}$, Cu$^{2+}$ and Ni$^{2+}$ than are the other treatments. Among common and comprehensive isotherm models, Langmuir was well fitted to evaluate the data obtained from adsorption experiments. This is a novel study to compare the effect of modified bentonites into both single and comparative solution for heavy metal sorption. The maximum Langmuir adsorption capacity of Cd$^{2+}$, Cu$^{2+}$ and Ni$^{2+}$ was 130.7, 94.4, and 83.06 as shown in SDS-B (40 mM) treatment. SDS-B treatments have the greatest affinity for Cd$^{2+}$, but the Na-B adsorbs Ni$^{2+}$ more than the other cations. Using SDS-B showed remarkable gain in enhancing the adsorption efficiency compared to the Na-B in both individual and competitive batch experiments.

Keywords: Anionic surfactant; Modified bentonite; Adsorption; Isotherm

1. Introduction

The protection of water resources from pollutants have been increasingly demanded to use of quality water in sanitary, drinking, agriculture, and trade in recent years. Heavy metals enter aquatic environments mainly through mining, plating, metallurgy, chemical plants, agriculture, and domestic wastewater [1]. Nowadays, water pollution by heavy metal became a serious environmental issues because of the stability in against chemical and biological degradations. Therefore, removal of heavy metals concentration from aqueous media is one of the major challenges in recent studies. It is important to choose environmentally friendly and low-cost procedures to reduce contaminations from water sources. Surface adsorption could be an efficacy way to transfer heavy metals from the aqueous to a solid phase. The choice of the best method of pollution removal depends on the type of contaminants, their concentration, equipment and maintenance and operational needs of the system. Many researchers suggested that the
application of a solid adsorbent with high ability to irreversible sorption of particular elements and limited under ambient conditions [1,2]. As a natural material, clays can be a special adsorbent for metal ions, because these compounds not only do not harm the environment as a natural substance, but also have been introduced as a natural and environmentally friendly adsorbent [3–5]. The electrocoagulation is critical for heavy metal removal processes, which depends in part on the availability of the affinity sites on the surface of the different adsorbents [6–9].

Clays have been suggested as an accessible, inexpensive, and eco-friendly absorbents with high specific surface area, chemical as well as mechanical stability, high cation exchange capacity (CEC), and Brønsted and Lewis acidity [10,11]. Bentonite mainly consisted of nanometer-scale smectite clay minerals, montmorillonite, and micrometer-scale macro-grains, chiefly quartz that is an expandable dioctahedral 2:1-layer silicate with negative charge containing 1.000 g L\textsuperscript{−1} concentration of Cd\textsuperscript{2+}, Cu\textsuperscript{2+}, and Ni\textsuperscript{2+} [22] and sodium dodecyl sulfate and hydroxyaluminosilicate to sorb Cd\textsuperscript{2+}, Cr\textsuperscript{6+}, and Cu\textsuperscript{2+} [23]. Guerra et al. [24] reformed montmorillonite clay for Hg removal by organo-functionalization with 3-aminopropyltriethoxysilane (APS).

Heavy metal adsorption by modified clays less studied by anionic surfactants like sodium dodecyl sulfate (SDS) [25]. Adsorption of heavy metals from the water by carbon nanosheet adsorbent were reported in different studies and they conducted that application of these absorbents can be a special adsorbent for metal ions, because these compounds not only do not harm the environment as a natural substance, but also have been introduced as a natural and environmentally friendly adsorbent [3–5]. The electrocoagulation is critical for heavy metal removal processes, which depends in part on the availability of the affinity sites on the surface of the different adsorbents [6–9].

In some studies, different surfactants used for modification of clay materials to improve adsorption performance [18,19]. Surfactants are included organic composites that encompass polar and non-polar characteristics and applied for adsorption. They were classified into three groups according to their resolution in water are cationic, anionic and non-ionic surfactants [20]. The effect of contact time, pH and adsorbent dosage of natural Slovak bentonites on copper adsorption were investigated in some studied [4,21]. In the study of Viglašová et al. [4] fast adsorption process and the equilibrium was obtained within 15 min and batch experiments well-fitted by Langmuir model of isotherm.

2. Experimental

2.1. Saturation of clay with Na\textsuperscript{+} cations

The bentonite powder was produced in national companies in Isfahan, Iran. Clay mineral fractionation (<2 µm) and saturation with NaCl (0.5 mol L\textsuperscript{−1}) was carried at first. Then, samples were washed with deionized water (DW).

After drying clay minerals that saturated with Na\textsuperscript{+}, test of negative chloride was measured using resuspension of AgNO\textsubscript{3}. Finally sorted in a desiccator until starting experiments [29].

Measurement of lattice constant of different crystalline materials was determined by X-ray diffractometry (XRD) with a Seifert 300 diffractometer with CuKa monochromatic radiation source (2θ = 10–70). Scanning electron microscope (SEM) measurements was conducted by a CamScanner MV2300. Also, Brunauer–Emmett–Teller (BET) analysis was measured to determine the specific surface areas and pore diameters was determined with a Micromeritics Chemisorption ASAP 2020 [30]. The Fourier-transform infrared spectroscopy (FTIR) was carried out for functional groups determining by the Na-B and SDS-B (20 mM) to determine the degree of surface activation.

2.2. SDS-Bentonite

The SDS was used as an anionic surfactant in this study to treat bentonite in different dosage. Thus, the 10, 20, and 40 Mm of SDS solution was prepared separately in 1 L of DW and combined with a mixture of 20 g of Na-bentonite and 5 mL acetone. Acetone was applied to decrease the stickiness of clays suspension and make it more convenient.

The combination was agitation for 2 h and then centrifuged to separate solid particles from the aqueous phase by filtration. Then, it was washed multiple times with distilled water in order to remove sorbed SDS on the surface [31].

2.3. Chemical properties of sodium dodecyl sulfate

The SDS \(\text{[CH}_2\text{CH}(\text{CH}_3)\text{SO}_4\text{Na}^-]\) was provided from Sigma-Aldrich Co. The clay was modified by the surfactant impregnation to change the structure of the clay and increase the adsorption capacity. A stock solution of heavy metals was bought from Merck (Darmstadt, Germany) and contain 1.000 g L\textsuperscript{−1} concentration of Cd\textsuperscript{2+}, Cu\textsuperscript{2+}, and Ni\textsuperscript{2+} obtained through dissolving appropriate the concentration of CdCl\textsubscript{2}H\textsubscript{2}O, CuCl\textsubscript{2} 2H\textsubscript{2}O and NiCl\textsubscript{2} 6H\textsubscript{2}O in DW.

2.4. Adsorption experiments

According to the standard conditions in previous studies to optimize the properties of natural bentonite [32], batch experiment was carried out in different concentration of Cd\textsuperscript{2+}, Cu\textsuperscript{2+}, and Ni\textsuperscript{2+} that varied from 25 to 600 mg L\textsuperscript{−1} added in 50 mL polyethylene tubes in 1:10 soil: solution ratio, in single and competitive solutions at 25°C temperature.

After 3 h in 1500 rpm shaking and centrifuging for 15 min, the mixture was filtered and the supernatant was kept for Cd\textsuperscript{2+}, Cu\textsuperscript{2+} and Ni\textsuperscript{2+} analyses by an inductively-coupled plasma mass spectrometry (Varian E-710). All experiments were performed in two replications.
The adsorption capacity of samples accompanied by different concentration of heavy metals was calculated and Langmuir and Freundlich were carried out for each isotherm. The Langmuir model was found for the monolayer sorption onto a limited number of surface while the Freundlich model was based on a heterogeneous surface sorption. In the following equations:

\[ q_e = \frac{(C_i - C_e)V}{M} \]  
(1)

\[ q_e = \frac{Q_{\text{max}}bC_e}{1 + bC_e} \]  
(2)

\[ q_e = \frac{Q_{\text{max}}}{C_e^{1/n}} \]  
(3)

where \( q_e \) is the adsorbed heavy metal at equilibrium (mg g\(^{-1}\)), \( V \) is the initial volume (mL) and \( M \) is the mass of adsorbent (g). The \( C_i \) and \( C_e \) are the initial and equilibrium concentration of heavy metals in solution (mg L\(^{-1}\)), respectively. The \( Q_{\text{max}} \) is the maximum adsorption capacity (mg g\(^{-1}\)), and \( b \) is the constant related to the affinity. \( K_f \) and \( n \) are indicators of adsorption capacity and intensity, respectively. \( Q_{\text{max}} \) and \( b \) can be determined from the linear plot of \( C_e = q_e \) vs. \( C_e \). The values of \( K_f \) and \( n \) were evaluated from the intercept and the slope, respectively, of the linear plot of \( \ln q_e \) vs. \( \ln C_e \) based on the experimental data.

3. Results and discussion

3.1. Modified bentonite properties

Based on the XRD and SEM analysis, bentonite consisted mainly of montmorillonite and quartz. The mean diameter of pores was 13.91 nm and BET was calculated 84.9 m\(^2\) g\(^{-1}\) for bentonite. The most cations in bentonite were frequently Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), and K\(^+\). Shown in Table 1 are the characteristics of natural Iranian bentonite [30]. The FTIR spectra of Na-B and SDS-B are presented in Fig. 1. The adsorption peaks in the 2,800–3,000 cm\(^{-1}\) regions correspond to an asymmetric- and symmetric stretch vibration of the H–C–H groups that are not present in Na-B, but they appear after SDS impregnation. Appearance of peaks around 2,900 cm\(^{-1}\) in SDS-B showed the C–H stretching and aromatic rings indicating the increase in functional groups in this absorbent. There is a bending vibration of the H–C–H groups formed after SDS modification. Between 1,625–1,750 cm\(^{-1}\) in the region from 1,400 to 1,500 cm\(^{-1}\), there is a vibrational stretch of the C=O functional group after the impregnation, depicted by the difference in peak intensity. Sulfate forms part of the structure of SDS, which reveals a successful impregnation [31,33].

3.2. Equilibrium sorption

The Langmuir and Freundlich parameters for sorption of Cd\(^{2+}\), Cu\(^{2+}\) and Ni\(^{2+}\) onto Na-B and SDS-B are listed in Table 2. Values of \( R \) show that the sorption data can match with both Langmuir and Freundlich models. The graphical finesses of adsorption isotherms for Na-B, SDS-B (10 mM), SDS-B (20 mM), and SDS-B (40 mM) are shown in Fig. 2. The sorption content and the concentration of equilibrium solution enhanced with increase of Cd\(^{2+}\), Cu\(^{2+}\) and Ni\(^{2+}\) (Fig. 2). The higher rate of sorption was observed in low Cd\(^{2+}\), Cu\(^{2+}\) and Ni\(^{2+}\) concentrations. The Cd\(^{2+}\), Cu\(^{2+}\) and Ni\(^{2+}\) percentage decreased with increase in Cd\(^{2+}\), Cu\(^{2+}\) and Ni\(^{2+}\) concentration, indicating that at low concentrations of Cd\(^{2+}\), Cu\(^{2+}\) and Ni\(^{2+}\) were sorbed, a greater proportion of the initial concentrations.

Both Langmuir and Freundlich models were fitted well with sorption data except for the adsorption of Cu\(^{2+}\) and Ni\(^{2+}\) onto SDS-Na (20 mM), which could not be described with Langmuir model (Table 2). The adsorption capacity improved, when Na-B was modified with an anionic surfactant to SDS-B (Fig. 2). Thus, the modification to Na-B by the anionic surfactant is an efficacy technique because the micelles of SDS substituted into the bentonite and it developed the functional groups of Na-B (Fig. 1). This cause to increase in cations adsorption capacity and led to improve in the surface properties of bentonite [34,35]. The SDS have been grafted into inner site of clay and the negative charge probably increased at clay surface which increased the potential of metal adsorption [22]. The similar results reported

Table 1
Characterization of natural bentonite (Merrikhpour and Jalali [30])

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>pH*</th>
<th>EC*</th>
<th>Na(^+)</th>
<th>K(^+)</th>
<th>Ca(^{2+})</th>
<th>Mg(^{2+})</th>
<th>Cl(^-)</th>
<th>HCO(_3^-)</th>
<th>CO(_3^{2-})</th>
<th>PO(_4^{3-})</th>
<th>NO(_3^-)</th>
<th>SO(_4^{2-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural bentonite</td>
<td>9.27</td>
<td>1.23</td>
<td>347.5</td>
<td>3.2</td>
<td>2.8</td>
<td>0.01</td>
<td>337.2</td>
<td>243.5</td>
<td>45.0</td>
<td>0.6</td>
<td>18.8</td>
<td>84.5</td>
</tr>
</tbody>
</table>

*Measured in 1:5 solid:liquid, solution (dS m\(^{-1}\)). The contact time was 24 h.
for sorption of Cu\(^{2+}\) and Zn\(^{2+}\) by SDS-montmorillonite adsorbents in another study [22]. After surface modification of clay by SDS, the surface of bentonite was covered by negatively charged dodecyl sulfate anions, which promote the increase of metal ions sorption [36].

Fig. 2 shows that the sorption of heavy metals reached at approximately 140 mg L\(^{-1}\) when SDS-B (40 mM) were applied to Cd sorption. It is concluded that the sorption of metal ions on SDS-B occurred using two mechanisms, ion-exchange and surface complexation [37]. During ion-exchange process, metal ions entered into inner surface of bentonite (and also of SDS-B) through pores and channels that could exchange by other sorbed cations. The rate of metal ions diffusion of increased in pores and then, it decreased when metal ions passed through small diameter having channels, and exactly during slow diffusion ion-exchange reactions occurred in channels [37]. Guerra et al. [24] showed an enhancement in the adsorption capacity in result of the physical and chemical changes on the clay surface when APS was applied. Vasudevan and Lakshmi [8] reported that the electrocoagulation process is mainly responsible for efficacy adsorption of Cd\(^{2+}\) from water the sorption was preferably fitting with Langmuir adsorption isotherm similar to the result of this study.

Because bentonite is naturally expandable with having the inner space of montmorillonite, the big anionic types such as SDS may become strongly fixed [31,38]. To adsorb ionic and complex forms of metals, the clay surface must have negatively charged sites, otherwise the metal ions must be replaced by cations that are adsorbed with weak bonds to the clay surface. Adsorption of cations on clays modified by anionic surfactant can be ascribed to the formation of cationic complex on clay surface [17]. Many researchers have studied the modification of clay with a mixture of two different surfactants for increase the organic contaminants sorption [39]. Modified-carboxy decyl triethyl ammonium bromide (CDTEA-Br)-montmorillonite is most likely supposed to absorb both Pb\(^{2+}\) and chlorobenzene [40]. Modified Kaolin with acetyl trimethyl ammonium (CTAB) cause to decrease Cu\(^{2+}\) and organic contaminations, like o-xylene and phenol [41]. Also, application of a novel absorbent (hexadecyltrimethylammonium-bentonite) for sorption of
U(IV) showed that the U(IV) sorption better fitted to the Langmuir adsorption isotherm.

### 3.3. Competitive adsorption

The maximum adsorption capacity of SDS-B followed the order of Cd > Cu > Ni for three studied heavy metals (Table 3 and Fig. 3). However, Evans reported different order for heavy metal sorption (Cu > Ni > Cd) and did not precisely convey the order of heavy metal electronegativity, which also alerted Cu (10–8.0) > Ni (10 –9.9) > Cd (10 –10.1) based on the $K_h$ as first hydrolysis constant [42]. Nevertheless, the more sorption potential for Cu occurred because of the high electronegativity of Cu compared to the Ni.

The Freundlich distribution coefficient ($K_f$) and constant ($n$) are presented the measures of the extent and energy of adsorption. Among the treatments, the value of $K_f$ for Cd$^{2+}$, Cu$^{2+}$ and Ni$^{2+}$ was the highest for SDS-B (40 mM). It is remarkable that SDS-B (40 mM) exhibited significantly higher adsorption affinities to Cd$^{2+}$, Cu$^{2+}$ and Ni$^{2+}$ (Table 2).

The mobility and adsorption of heavy metals from solutions have influenced by complexation of heavy metals in solutions and heavy metals competition for the adsorbent surface, the adsorption process of Cd$^{2+}$, Cu$^{2+}$, and Ni$^{2+}$ onto SDS-B in competitive solution was studied to determine the effect of another metal on quantity of adsorption. The results of other studies have revealed that among ion exchange, coagulation-flocculation, chemical precipitation, evaporation, membrane filtration, electrochemical functions, and adsorption, clays with adsorption process with low-cost, flexibility, ease of operation considered as an efficiency adsorbent for heavy metals in water [43]. Bentonite is able to adsorb hydrophobic functional groups, anionic, and cationic ions in a competitive solution [44]. For example, Cr(VI) and Mo(VI) was effectively adsorbed by cetyl pyridinium bromide (CPB)-modified bentonite from water [45]. In another study on natural and activated bentonite by Ibigbami et al. [46], adsorption capacities and intensity of Freundlich equation are more in activated bentonite than natural, showing that the tendency for multilayer adsorption is enhanced by acidified activation, which also improved the natural clay’s surface morphology like what happened in our study for SDS-B.

### 3.4. Effect of pH on heavy metal adsorption

The pH is an important parameter in the competitive adsorption process of heavy metals [47]. The adsorptions of Cd$^{2+}$, Cu$^{2+}$, and Ni$^{2+}$ onto Na-B and SDS-B were conducted at pH ranged from 3 to8. Fig. 4. The figure illustrated the amounts of Cd$^{2+}$, Cu$^{2+}$, and Ni$^{2+}$ adsorbed onto Na-B, SDS-B (10 mM), SDS-B (20 mM), and SDS-B (40 mM) at various pH values.

The sorption of Cd$^{2+}$, Cu$^{2+}$ and Ni$^{2+}$ on bentonite is obviously affected by pH values. According to Fig. 4, competitive sorption process occurs at acidic pH between metal ions and H$. In this pH, more H$ ions compete with Cd$^{2+}$, Cu$^{2+}$ and Ni$^{2+}$ led to Cd$^{2+}$, Cu$^{2+}$ and Ni$^{2+}$ adsorption on the surface;
while, low amount of adsorption obtained in pH < 5. With the increase in pH, the positive charge decreased and the number of negatively charged sites would increase on the adsorbent surface. Hence, acidic condition increased adsorption capacity of both adsorbents to remove Cd	extsuperscript{2+}, Cu	extsuperscript{2+}, and Ni	extsuperscript{2+} from solutions through surface complex reactions [48]. Castro-Castro et al. observed that highest Cr(VI) adsorption between 3.0 to 4.0 pH. For the pH of >2.5 and >5 caused to decrease in the content of Cr(VI) adsorption [49]. However, in an alkaline condition, concentration of heavy metals decreased because of the formation of insoluble complexes with absorbents it is not originated from sorption process [50]. According to the previous researches, it is suggested that the range of pH between 5 and 6 is more efficacy for effective sorption of the heavy metals [51]. In this study, the major factors to facilitate adsorption process is amount of adsorbent and the pH of solution which was also confirmed in other studies [49].

### 3.5. Heavy metal adsorption in different pH

The adsorption efficiency of Cd	extsuperscript{2+}, Cu	extsuperscript{2+}, and Ni	extsuperscript{2+} onto Na-B and SDS-B are shown in Table 4 in various pH. The SDS-B is a more effective sorbent for removing metal ions from aqueous solutions. The increase of Cd	extsuperscript{2+}, Cu	extsuperscript{2+}, and Ni	extsuperscript{2+} sorption on clays saturated with Na	extsuperscript{+}, are consist with increasing pH and may be attributed to the surface characteristics of Na-clay and the dissociation of functional groups [32]. The surface of Na-clay has numerous sorption sites that are participated in positively adsorption at low pH values because of the protonation reaction on the surfaces (i.e., SOH + H\textsuperscript{+} ⇔ SOH\textsuperscript{2+}). The electrostatic desorption is occurring among ionic forms of metals and positively charged surface sites such as SOH\textsuperscript{2+} on Na-clay surface led to the low sorption proximity of Cd	extsuperscript{2+}, Cu	extsuperscript{2+}, and Ni	extsuperscript{2+}. At alkaline pH, Na-clay surface became negatively charged when the deprotonation process is performed (i.e., SOH ⇔ SO\textsuperscript{-} + H\textsuperscript{+}) and electrostatic desorption decreased with the increasing pH due to the reduction of positive charge density on the sorption edges, enhancing the sorption of the positively charged Cd	extsuperscript{2+}, Cu	extsuperscript{2+}, and Ni	extsuperscript{2+} ions by the electrostatic force of sorption [32].

The result was also similar to the results of a study by Tohdee and Asadollah [52] that observed the modified bentonite had significantly improved adsorption capacities for Cu	extsuperscript{2+} and Zn	extsuperscript{2+} approximately 2.5- and 2.0-fold improvements over natural bentonite, respectively. The best fit with experimental data was also obtained in Langmuir isotherm.
4. Conclusion

Clays have been known as an adsorbent with wide variety of active sites on the surface, like ion exchange sites. This activity, however, depends on many other environmental factors especially pH. The modification of clays by saturating with Na⁺ cations and treating with SDS had a considerable effect on the structural properties and enhanced their adsorption capacities. It was confirmed by FTIR analysis and the relevant adsorption
studies that the successful impregnation of bentonite is evident throughout the study. The adsorption affinity of SDS-B for all studied cations is higher than that Na-B. The SDS-B proved to be an effective adsorbent to remove heavy metals and can be utilized for wastewater purification. It must be noted that the modification of natural bentonite by surfactant is a very easy and inexpensive process to apply and it does not increase the cost of the sorbent.

Acknowledgment

The authors thank all those who contributed to this project. We would like to thank the Vice-Chancellor for Education and research of Sayyed Jamaledin Asadabadi University for approving this study.

References


