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

Hajar Merrikhpour<sup>a,\*</sup>, Sara Mobarakpour<sup>b</sup>, Seyedeh Bahareh Azimi<sup>c</sup>

*a Department of Agriculture, Sayyed Jamaleddin Asadabadi University, Asadabad 6541861841, Iran, emails: merrikhpour@sjau.ac.ir/hajar.merrikhpour@gmail.com*

*b M.Sc. in Environmental Pollution, Islamic Azad University, Hemedan 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<sup>2+</sup>) and nickel (Ni<sup>2+</sup>) 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<sup>2+</sup> (25–600 mg L<sup>-1</sup>) 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<sup>2+</sup> 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<sup>2+</sup> 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

<sup>\*</sup> Corresponding author.

<sup>1944-3994/1944-3986 © 2022</sup> Desalination Publications. All rights reserved.

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 silicates which contains negative charge [12,13]. Also, montmorillonite known as a clay with high CEC, specific expandability, and specific surface area, which has a high capacity for ionic and polar compounds adsorption [14,15]. However, clay minerals have limited capacity for metal adsorption and may be improved with some remediators before application for treatment of aqueous or wastewater systems to raise adsorption capacity [11,16,17].

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.

Surfactant-modified montmorillonite are used as an effective adsorbent to remove  $Cu^{2+}$  and  $Zn^{2+}$  [22] and sodium dodecyl sulfate and hydroxyaluminosilicate to sorb  $Cd^{2+}$  $Cr^{3+}$ , and  $Cu^{2+}$  [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 cause to effectively remove heavy metals from solutions [26–28]. Despite the new modifiers with the available surface, more research is still required to raise the surface capacity of these materials. As metal ions are cationic in nature, an anionic surfactant, like SDS, is chosen to evaluate the adsorption capacity of cadmium  $(Cd^{2+})$ , copper  $(Cu^{2+})$  and nickel  $(Ni^{2+})$  onto bentonite in this study.

This is a novel study to compare individual and competitive sorption of  $Cd^{2+}$ ,  $Cu^{2+}$ , and  $Ni^{2+}$  simultaneously by Na-B and SDS-B in different pH values. The objective of this study is to modify surface properties and investigate capacity of natural Iranian bentonite to remove  $Cd^{2+}$ ,  $Cu^{2+}$ , and  $Ni^{2+}$ sorption from aqueous solutions.

## **2. Experimental**

#### *2.1. Saturation of clay with Na+ cations*

The bentonite powder was produced in national companies in Isfahan, Iran. Clay mineral fractionation  $(2 \mu m)$ and saturation with NaCl (0.5 mol L−1) was carried at first. Then, samples were washed with deionized water (DW). After drying clay minerals that saturated with Na, test of negative chloride was measured using resuspension of AgNO<sub>3</sub>. 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 CuKα monochromatic radiation source ( $2h\theta = 10-70$ ). 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 agitated 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  $[\text{CH}_3(\text{CH}_2)_{11} \text{SO}_4^- \text{Na}^+]$  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<sup>-1</sup> concentration of Cd<sup>2+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup> obtained through dissolving appropriate the concentration of CdCl<sub>2</sub> H<sub>2</sub>O, CuCl<sub>2</sub> 2H<sub>2</sub>O and NiCl<sub>2</sub> 6H<sub>2</sub>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  $Cd^{2+}$ ,  $Cu<sup>2+</sup>$ , and Ni<sup>2+</sup> that varied from 25 to 600 mg L<sup>-1</sup> 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  $Cd^{2+}$ ,  $Cu^{2+}$  and  $Ni^{2+}$  analyses by an inductivelycoupled 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:

$$
\text{Linear: } q_e = \frac{\left(C_i - C_e\right)V}{M} \tag{1}
$$

$$
\text{Freundlich: } q_e = \frac{Q_{\text{max}} b C_e}{1 + b C_e} \tag{2}
$$

$$
Langmuir: q_e = K_f C_e^{1/n}
$$
\n(3)

where *qe* 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) and  $b$  the constant related to the affinity.  $K_a$ 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<sup>2</sup>  $g^{-1}$  for bentonite. The most cations in bentonite were frequently  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , and K<sup>+</sup>. 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<sup>-1</sup> 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<sup>-1</sup> 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<sup>-1</sup> in the region from 1,400 to 1,500 cm<sup>-1</sup>, 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  $Ni<sup>2+</sup>$  (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  $Ni<sup>2+</sup>$  percentage decreased with increase in Cd<sup>2+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup> 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  $Cu<sup>2+</sup>$  and Ni2+ 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



Fig. 1. Infrared spectra of Na-bentonite (Na-B) and SDSbentonite (SDS-B).

Table 1

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

Absorbent	Solution ions* (mg $L^{-1}$ )											
	$pH^*$	$EC^*$	Na <sup>+</sup>	$K^*$	$Ca^{2+}$	$Mg^{2+}$ Cl <sup>-</sup>		HCO <sub>2</sub>	CO <sub>2</sub> <sup>2</sup>	$\mathrm{PO}_4^{3-}$	NO <sub>2</sub>	SO <sub>4</sub>
Natural bentonite	9.27	1.23	347.5	3.2	2.8	0.01	337.2	243.5	45.0	0.6	18.8	84.5

\*Measured in 1:5 solid:liquid, solution (dS  $m^{-1}$ ). The contact time was 24 h.



Fig. 2. Adsorption isotherms of Cd<sup>2+</sup>, Cu<sup>2+</sup>, and Ni<sup>2+</sup> and fitted model in onto Na-B and SDS-B (10, 20, and 40 mM).

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<sup>2+</sup> 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

Langmuir	$Ni2+$					$Cu2+$			$Cd2+$				
	$Q_{\rm max}$ $(mg g^{-1})$	$b(Lg^{-1})$	$\boldsymbol{R}$	<b>SE</b>	$Q_{\text{max}}$ (mg g <sup>-1</sup> )	$b(Lg^{-1})$	R	<b>SE</b>	$Q_{\text{max}}$ (mg g <sup>-1</sup> )	$b(Lg^{-1})$	R	<b>SE</b>	
$Na-B$	45.9	0.01	0.99	0.63	33.4	0.01	0.99	0.79	37.00	0.06	0.99	0.66	
$SDS-B (10 \text{ mM})$	55.4	0.01	0.98	3.4	98.2	0.005	0.97	5.8	186.3	0.002	0.96	10.1	
$SDS-B (20 mM)$						$\qquad \qquad$		$\qquad \qquad$	147.7	0.007	0.98	6.9	
$SDS-B (40$ mM)	83.06	0.006	0.98	4.2	94.4	0.12	0.99	4.3	130.7	0.09	0.97	12.7	
Freundlich	$Kf$ (L $g-1$ )	$\boldsymbol{n}$	$\boldsymbol{R}$	<b>SE</b>	$K_{f}$ (L $g^{-1}$ )	$\,n$	R	SE	$Kf$ (L $g-1$ )	$\,n$	$\boldsymbol{R}$	<b>SE</b>	
$Na-B$	1.4	1.5	0.99	0.92	1.4	1.7	0.98	1.5	3.9	1.9	0.98	1.6	
$SDS-B (10 \text{ mM})$	6.1	2.9	0.99	2.3	3.4	2.0	0.99	3.5	3.3	1.7	0.98	6.9	
$SDS-B (20 mM)$	0.04	0.86	0.99	2.5	0.27	1.1	0.98	5.5	5.1	1.9	0.98	8.9	
$SDS-B (40 \text{ mM})$	3.0	2.0	0.97	5.7	25.8	4.3	0.96	10.8	29.5	3.7	0.92	20.8	

Langmuir and Freundlich sorption isotherm parameters for  $Cd^{2+}$ ,  $Cu^{2+}$  and Ni<sup>2+</sup> onto Na-B and SDS-B

Table 3 Langmuir sorption isotherm parameters for Cd<sup>2+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup> onto SDS-B in a competitive adsorption solution



U(IV) showed that the U(IV) sorption better fitted to the Langmuir adsorption isotherm.

#### *3.3. Competitive adsorption*

Table 2

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 *Kh* 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  $(K<sub>\rho</sub>)$  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<sup>2+</sup> 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<sup>2+</sup> 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<sup>+</sup>. In this pH, more H<sup>+</sup> ions compete with  $Cd^{2+}$ ,  $Cu^{2+}$ and  $Ni^{2+}$  led to  $Cd^{2+}$ ,  $Cu^{2+}$  and  $Ni^{2+}$  adsorption on the surface;



Fig. 3. Competitive adsorption of  $Cd^{2+}$ , Cu<sup>2+</sup> and Ni<sup>2+</sup> onto SDS-B in different concentration (10, 20, and 40 mM).

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  $Cd^{2+}$ ,  $Cu^{2+}$ , and Ni<sup>2+</sup> 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  $Cd^{2+}$ ,  $Cu^{2+}$ , and  $Ni^{2+}$  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  $Cd^{2+}$ ,  $Cu^{2+}$ , and  $Ni<sup>2+</sup>$  sorption on clays saturated with Na<sup>+</sup>, 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.,  $SOH + H^+ \Leftrightarrow SOH_2^*$ ). The electrostatic desorption is occurring among ionic forms of metals and positively charged surface sites such as  $SOH<sub>2</sub><sup>+</sup>$  on Na-clay surface led to the low sorption proximity of  $Cd^{2+}$ ,  $Cu^{2+}$ , and Ni<sup>2+</sup>. At alkaline pH, Na-clay surface became negatively charged when the deprotonation process is performed (i.e., SOH  $\Leftrightarrow$  SO<sup>−</sup> + H<sup>+</sup>) 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<sup>2+</sup>, Cu<sup>2+</sup>, and Ni<sup>2+</sup> 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  $Cu<sup>2+</sup>$  and  $Zn<sup>2+</sup>$  approximately 2.5- and 2.0-fold improvements over natural bentonite, respectively. The best fit with experimental data was also obtained in Langmuir isotherm.



Fig. 4. Effect of pH on the adsorption of  $Cd^{2+}$ ,  $Cu^{2+}$ , and Ni<sup>2+</sup> onto Na-B and SDS-B (10, 20, and 40 mM).





\*Since Cu<sup>2+</sup> has been precipitated in pH above 7, the maximum studied pH about Cu<sup>2+</sup> was 7.

# **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 Jamaleddin Asadabadi University for approving this study.

#### **References**

- [1] J. Yang, B. Hou, J. Wang, B. Tian, J. Bi, N. Wang, X. Li, X. Huang, Nanomaterials for the removal of heavy metals from wastewater, Nanomaterials, 9 (2019) 424, doi: 10.3390/ nano9030424.
- [2] Ş. Kubilay, R. Gürkan, A. Savran, T. Şahan, Removal of Cu(II), Zn(II) and Co(II) ions from aqueous solutions by adsorption onto natural bentonite, Adsorption, 13 (2007) 41–51.
- [3] M. Galamboš, P. Suchánek, O. Rosskopfová, Sorption of anthropogenic radionuclides on natural and synthetic inorganic sorbents, J. Radioanal. Nucl. Chem., 293 (2012) 613–633.
- [4] E. Viglašová, M. Daňo, M. Galamboš, A. Krajňák, O. Rosskopfová, P. Rajec, Investigation of Cu(II) adsorption on Slovak bentonites and illite/smectite for agricultural applications, J. Radioanal. Nucl. Chem., 314 (2017) 2425–2435.
- [5] A. Krajňák, L. Pivarčiová, O. Rosskopfová, M. Galamboš, P. Rajec, Adsorption of nickel on rhyolitic Slovak bentonites, J. Radioanal. Nucl. Chem., 304 (2015) 587–593.
- [6] R. Kamaraj, P. Ganesan, J. Lakshmi, S. Vasudevan, Removal of copper from water by electrocoagulation process—effect of alternating current (AC) and direct current (DC), Environ. Sci. Pollut. Res., 20 (2013) 399–412.
- [7] S. Vasudevan, J. Lakshmi, Effects of alternating and direct current in electrocoagulation process on the removal of cadmium from water – a novel approach, Sep. Purif. Technol., 80 (2011) 643–651.
- [8] S. Vasudevan, J. Lakshmi, Process conditions and kinetics for the removal of copper from water by electrocoagulation, Environ. Eng. Sci., 29 (2012a) 563–572.
- [9] S. Vasudevan, J. Lakshmi, G. Sozhan, Optimization of electrocoagulation process for the simultaneous removal of mercury, lead, and nickel from contaminated water, Environ. Sci. Pollut. Res., 19 (2012b) 2734–2744.
- [10] K. Tanabe, Solid Acid and Base Catalysis, J.R. Anderson, M. Boudart, Eds., Catalysis Science and Technology, Springer Verlag, New York, 1981, p. 231.
- [11] M.E. Jiménez-Castañeda, D.I. Medina, Use of surfactantmodified zeolites and clays for the removal of heavy metals from water, Water, 9 (2017) 235, doi: 10.3390/w9040235.
- [12] A. Perry, Cheryl McCoy, Eds., Living Clay Natures Own Miracle Cure, 1st ed., Perry Productions, Kyle, Texas, 2006.
- [13] F. Bergaya, G. Lagaly, General Introduction: Clays, Clay Minerals, and Clay Science, F. Bergaya, B.K.G. Theng, G. Lagaly, Eds., Handbook of Clay Science: Developments in Clay Science, Vol. 1, Elsevier, Amsterdam, 2006, pp. 1–18.
- [14] G.A. Ikhtiyarova, A.S. Özcan, Ö. Gök, A. Özcan, Characterization of natural- and organobentonite by XRD, SEM, FT-IR and thermal analysis techniques and its adsorption behaviour in aqueous solutions, Clay Miner., 47 (2012) 31–44.
- [15] S. Parolo, A. Lisa, A. Gentilini, A.M. Di Blasio, S. Barlera, E.B. Nicolis, G.B. Boncoraglio, E.A. Parati, S. Bione, Characterization of the biological processes shaping the genetic

structure of the Italian population, BMC Genet., 16 (2015) 132, doi: 10.1186/s12863-015-0293-x.

- [16] L.B. de Paiva, A.R. Morales, F.R. Valenzuela Díaz, Organoclays: properties, preparation and applications, Appl. Clay Sci., 42 (2008) 8–24.
- [17] Z.Z. Zhang, D.L. Sparks, N.C. Scrivner, Sorption and desorption of quaternary amine cations on clays, Environ. Sci. Technol., 27 (1993) 1625–1631.
- [18] Y. Xi, M. Mallavarapu, R. Naidu, Preparation, characterization of surfactants modified clay minerals and nitrate adsorption, Appl. Clay Sci., 48 (2010) 92–96.
- [19] R. Mudzielwana, M.W. Gitari, P. Ndungu, Performance evaluation of surfactant modified kaolin clay in As(III) and As(V) adsorption from groundwater: adsorption kinetics, isotherms and thermodynamics, Heliyon, 5 (2019) e02756, doi: 10.1016/j.heliyon.2019.e02756.
- [20] S. Ismadji, F.E. Soetaredjo, A. Ayucitra, Clay Materials for Environmental Remediation, Springer Briefs in Green Chemistry for Sustainability, Springer, Cham, 2015, pp. 39–56.
- [21] A. Krajňák, E. Viglašová, M. Galamboš, L. Krivosudský, Application of HDTMA-intercalated bentonites in water waste treatment for U(VI) removal, J. Radioanal. Nucl. Chem., 314 (2017) 2489–2499.
- [22] S.-H. Lin, R.-S. Juang, Heavy metal removal from water by sorption using surfactant-modified montmorillonite, J. Hazard. Mater., 92 (2002) 315–326.
- [23] Y. Liu, P.X. Wu, Z. Dang, D. Ye, Heavy metal removal from water by adsorption using pillared montmorillonite, Acta Geol. Sin., 80 (2006) 219–225.
- [24] D.L. Guerra, C. Airoldi, R. de Sousa Viana, Performance of modified montmorillonite clay in mercury adsorption process and thermodynamic studies, Inorg. Chem. Commun., 11 (2008) 20–23.
- [25] P. Li, M. Ishiguro, Adsorption of anionic surfactant (sodium dodecyl sulfate) on silica, J. Soil Sci. Plant Nutr., 62 (2016) 223–229.
- [26] M.A. Tofighy, T. Mohammadi, Adsorption of divalent heavy metal ions from water using carbon nanotube sheets, J. Hazard. Mater., 185 (2011) 140–147.
- [27] R. Baby, B. Saifullah, M.Z. Hussein, Carbon nanomaterials for the treatment of heavy metal-contaminated water and environmental remediation, Nanoscale Res. Lett., 14 (2019) 341, doi: 10.1186/s11671-019-3167-8.
- [28] C. Rodríguez, S. Briano, E. Leiva, Increased adsorption of heavy metal ions in multi-walled carbon nanotubes with improved dispersion stability, Molecules, 25 (2020) 3106, doi: 10.3390/ molecules25143106.
- [29] L. Zhang, L. Luo, S.H. Zhang, Adsorption of phenanthrene and 1,3-dinitrobenzene on cation-modified clay minerals, Colloids Surf., A, 377 (2011) 278–283.
- [30] H., Merrikhpour, M. Jalali, Sorption processes of natural Iranian bentonite exchanged with  $C\hat{d}^{2+}$ ,  $Cu^{2+}$ , Ni<sup>2+</sup>, and Pb<sup>2+</sup> cations, Chem. Eng. Commun., 200 (2013) 1645–1665.
- [31] E. Fosso-Kankeu, F. Waanders, N. Lemmer, R.H. Steyn, Surfactant Impregnated Bentonite Clay for the Removal of Heavy Metals from Solution, 9th Int'l Conference on Advances in Science, Engineering, Technology & Waste Management (ASETWM-17), Parys, South Africa, 2017, pp. 27–28.
- [32] S. Yang, D. Zhao, H. Zhang, S. Lu, L. Chen, X. Yu, Impact of environmental conditions on the sorption behavior of Pb(II) in Na-bentonite suspensions, J. Hazard. Mater., 183 (2010) 632–640.
- [33] C. del Hoyo, C. Dorado, M.S. Rodríguez-Cruz, M.J. Sánchez-Martín, Physico-chemical study of selected surfactant-clay mineral systems, J. Therm. Anal. Calorim., 94 (2008) 227–234.
- [34] K.O. Adebowale, I.E. Unuabonah, B.I. Olu-Owolabi, The effect of some operating variables on the adsorption of lead and cadmium ions on kaolinite clay, J. Hazard. Mater., 134 (2006) 130–139.
- [35] K. Tohdee, L. Kaewsichan, Asadullah, Potential of BCDMACl modified bentonite in simultaneous adsorption of heavy metal Ni(II) and humic acid, J. Environ. Chem. Eng., 6 (2018) 5616–5624.

- [36] M. Andrunik, T. Bajda, Modification of bentonite with cationic and nonionic surfactants: structural and textural features, Materials, 12 (2019) 3772, doi: 10.3390/ma12223772.
- [37] L.R. Harutyunyan, L.S. Tangamyan, R.S. Harutyunyan, Sorption of  $Co^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ , Mn<sup>2+</sup> metal ions from aqueous solutions on anionic surfactant-modified bentonite, Chem. Biol., 53 (2019) 81–85.
- [38] R.P. Singh, J.P. Rawat, R. Kumar, Effect of cationic, non-ionic and anionic surfactants on the adsorption of carbofuran on three different types of Indian soils, Adsorpt. Sci. Technol., 18 (2000) 333, doi: 10.1260/0263617001493477.
- [39] A. Gil, L. Santamaría, S.A. Korili, M.A. Vicente, L.V. Barbosa, S.D. de Souza, L. Marçal, E.H. de Faria, K.J. Ciuffi, A review of organic-inorganic hybrid clay based adsorbents for contaminants removal: synthesis, perspectives and applications, J. Environ. Chem. Eng., 9 (2021) 105808, doi: 10.1016/j.jece.2021.105808.
- [40] G. Sheng, S.A. Boyd, S. Xu, A dual function organoclay sorbent for lead and chlorobenzene, Soil Sci. Soc. Am. J., 63 (1999) 73–78.
- [41] A.S. Sayed, Removal of toxic pollutants from aqueous solutions by adsorption onto organo-kaolin, Carbon Lett., 10 (2009) 305–313.
- [42] R.C. Evans, An Introduction to Crystal Chemistry, Cambridge University Press, London, 1966.
- [43] D. Lakherwal, Adsorption of heavy metals: a review, Int. J. Environ. Res. Dev., 4 (2014) 41–48.
- [44] V. Dimos, K.J. Haralambous, S. Malamis, A review on the recent studies for chromium species adsorption on raw and modified natural minerals, Crit. Rev. Env. Sci. Technol., 42 (2012) 1977–2016.
- [45] A.A. Atia, Adsorption of chromate and molybdate by cetylpyridinium bentonite, Appl. Clay Sci., 41 (2008) 73–84.
- [46] T.B. Ibigbami, A.O. Adeola, D.B. Olawade, O.T. Ore, B.O. Isaac, A.A. Sunkanmi, Pristine and activated bentonite for toxic metal removal from wastewater, Water Pract. Technol., 17 (2022) 784–797.
- [47] L.P. Cruz-Lopes, M. Macena, B. Esteves, R.P.F. Guiné, Ideal pH for the adsorption of metal ions  $Cr^{6+}$ , Ni<sup>2+</sup>, Pb<sup>2+</sup> in aqueous solution with different adsorbent materials, Open Agric., 6 (2021) 115–123.
- [48] P. Tan, J. Sun, Y. Hu, Z. Fang, Q. Bi, Y. Chen, J. Cheng, Adsorption of  $Cu^{2+}$ ,  $Cd^{2+}$  and  $Ni^{2+}$  from aqueous single metal solutions on graphene oxide membranes, J. Hazard. Mater., 297 (2015) 251–260.
- [49] J.D. Castro-Castro, I.F. Macías-Quiroga, G.I. Giraldo-Gómez, N.R. Sanabria-González, Adsorption of Cr(VI) in aqueous solution using a surfactant-modified bentonite, The Sci. World J., 2020 (2020) 3628163, doi: 10.1155/2020/3628163.
- [50] A.G. Caporale, A. Violante, Chemical processes affecting the mobility of heavy metals and metalloids in soil environments, Curr. Pollut. Rep., 2 (2016) 15–27.
- [51] R. Malik, N. Saini, S. Ahlawat, S. Singhal, S. Lata, Convenient and efficient elimination of heavy metals from wastewater using smart pouch with biomaterial, Pollution, 5 (2019) 13–31.
- [52] K. Tohdee, L. Kaewsichan, Asadullah, Enhancement of adsorption efficiency of heavy metal Cu(II) and Zn(II) onto cationic surfactant modified bentonite, J. Environ. Chem. Eng., 6 (2018) 2821–2828.