

Arsenic Contamination of Groundwater a Grave Concern: Novel Clay-based Materials for Decontamination of Arsenic (V)

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Abstract

Arsenic is a highly toxic element, and its contamination is widespread around the world. The natural materials with high selectivity and efficiency toward pollutants are important in wastewater treatment technology. In this study, the mesoporous synthetic hectorite was synthesized by facile hydrothermal crystallization of gels comprising silica, magnesium hydroxide, and lithium fluoride. Additionally, the naturally available clay was modified using zirconium at room temperature. Both synthetic and modified natural clays were employed in the removal of arsenate from aquatic environments. The materials were fully characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), and Fourier transform-infrared (FT-IR) analyses. The synthesized materials were used to remove arsenic (V) under varied physicochemical conditions. Both materials, i.e., Zr-bentonite and Zr-hectorite, showed high percentage removal of arsenic (V) at lower pH, and the efficiency decreased in an alkaline medium. The equilibrium-state sorption data agrees well with the Langmuir and Freundlich adsorption isotherms, and the maximum sorption capacity is found to be 4.608 and 2.207 mg/g for Zr-bentonite and Zr-hectorite, respectively. The kinetic data fits well with the pseudo-second order kinetic model. Furthermore, the effect of the background electrolytes study indicated that arsenic (V) is specifically sorbed at the surface of these two nanocomposites. This study demonstrated that zirconium intercalated synthetic hectorite as well as zirconium modified natural clays are effective and efficient materials for the selective removal of arsenic (V) from aqueous medium.

Keywords: *Arsenic (V), Natural clay, Synthetic hectorite, Intercalated zirconium clay, Nanocomposite*

1. Introduction

Arsenic is a toxic element widely distributed in human surroundings. Arsenic pollution has been reported from various countries, which are mainly due to the natural weathering and anthropogenic activities[1]. The presence of arsenic in aquatic environment has been reported from many countries in Europe, North and South America continents and several countries in Asia[2]. The groundwater in south and East Asian countries are found to have higher content of arsenic compared to other countries[2,3]. Different kinds of arsenic compounds (inorganic and organic) having varied oxidation states generally occur in the terrestrial aquatic environment. Arsenite (As(III)) and arsenate (As(V)) are commonly detected and their input in environmental contamination is higher than other arsenic species[4]. The human body receives arsenic mostly through the diets and causes several complications in various organs of the body[5,6]. Gastrointestinal discomfort, vomiting, anuria,

convulsions, skin lesions, and blackfoot diseases are the most common adverse effects of arsenic in the human body[7,8].

Arsenic contamination is a common issue across the globe, and numerous researchers are working on the development of techniques which could be efficiently utilized to eliminate arsenic from water bodies. Removal of arsenic was carried out via different techniques such as flocculation-sedimentation, adsorption, ion exchange membrane, etc.[9,10]. Of all these techniques, adsorption is found to be efficient and low cost for its operation. Also, adsorption techniques involve robust operation, cost effectiveness and choice of materials, sometimes, makes it sustainable[11]. Due to these reasons, adsorption techniques are employed extensively for arsenic remediation and many materials are reported to remove arsenic from aqueous media effectively. Activated carbon that was obtained from different raw materials is useful sorbing materials for the attenuation of arsenic [12,13,14]. Similarly, the indigenous clay is an interesting option due to the low cost and high stability. Clays are naturally abundant and possess distinguished properties that allow their application in various wastewater treatment techniques. Moreover, the porous clay structure is known as a natural filter medium. Recent studies have shown that zirconium oxide possesses a high affinity to adsorb arsenic[15-17]. Several researchers immobilized the zirconium into the host materials such as granular activated carbon[18], sand[19], metal organic frame-

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work (MOF)[20], sodium alginate composite[21], oxygen-rich-poly-bisvanillinitrile[22] activated charcoal[23], polyphenylsulfone/cellulose acetate hollow fiber membranes[24] etc. and then employed the modified material for removal of arsenic from aqueous medium. Therefore, it is interesting to intercalate the Zr within the interspace of natural and synthetic clay. Further, the Zr-intercalated clay materials were employed in the efficient elimination of arsenic (V) from aquatic environments. The parametric studies enabled to deduce the mechanism involved at the solid/solution interface in the sorption studies.

2. Materials and methods

Natural bentonite was used as starting natural clay materials for preparing nanocomposite. Zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) was used as the zirconium source. The Zr solution is prepared by considering the cation exchange capacities of clay. The incorporation of Zr to bentonite was carried out under microwave irradiation with continuous stirring for 1 h. In addition, the mesoporous synthetic hectorite was synthesized by hydrothermal crystallization of gels similar to the reported method[25]. In typical synthesis, reactants in the molar ratios of $LiF:MgO:SiO_2$ as 0.2 :1.0 :1.5 were refluxed for 48 h and finally produced hectorite. In order to synthesize the Zr loaded bentonite/hectorite, 0.066 M of zirconium oxychloride was used for incorporation of Zr in natural and synthetic clay following the same procedure as demonstrated before for natural bentonite.

The materials were characterized by a Scanning electron microscope (FE-SEM-Model: SU-70 Hitachi, Japan) with an energy dispersive X-ray spectroscopy (EDX) system. Other instruments such as X-ray diffraction (XRD) instrument (PANalytical, Netherland; Model X'Pert PRO MPD) and Fourier transform-infrared spectrometry (FT-IR) (Bruker, Tensor 27, USA) were used for characterization.

Batch experiments are conducted to evaluate the effect of solution pH, initial arsenic (V) concentration, contact time, dose of the adsorbent, and background electrolyte ($NaNO_3$) concentrations on arsenic (V) removal using Zr-Bentonite and Zr-Hectorite solids. The influence of change in solution pH was studied using the arsenic (V) concentration of 6.0 mg/L from pH 2.0 to 9.0. The concentration dependent studies were performed between the initial arsenic (V) concentrations from 2.0 to 26.0 mg/L at pH: 5.0. The time dependence sorption of arsenic (V) by both the solids was conducted varying the contact time up to 600 min at initial arsenic (V) concentration of 5.0 mg/L and pH 5.0. Further, the effect of dose of the nanocomposite material and influence of background electrolyte concentrations were studied using arsenic (V) concentration of 5.0 mg/L at pH 5.0. For all these experiments, the dose of the solid material was maintained at 5.0 g/L and the time given for equilibration between solid and solution was 15 h.

3. Results and discussion

3.1. Characterization of materials

The SEM micrographs of Zr-Bentonite and Zr-Hectorite are presented in Fig. 1. The SEM micrographs showed that the Zr-bentonite

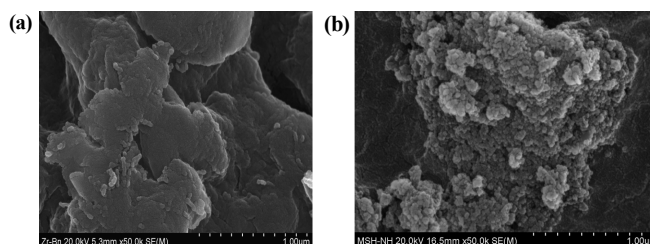


Figure 1. SEM images of (a) Zr-Bentonite, and (b) Zr-Hectorite solids.

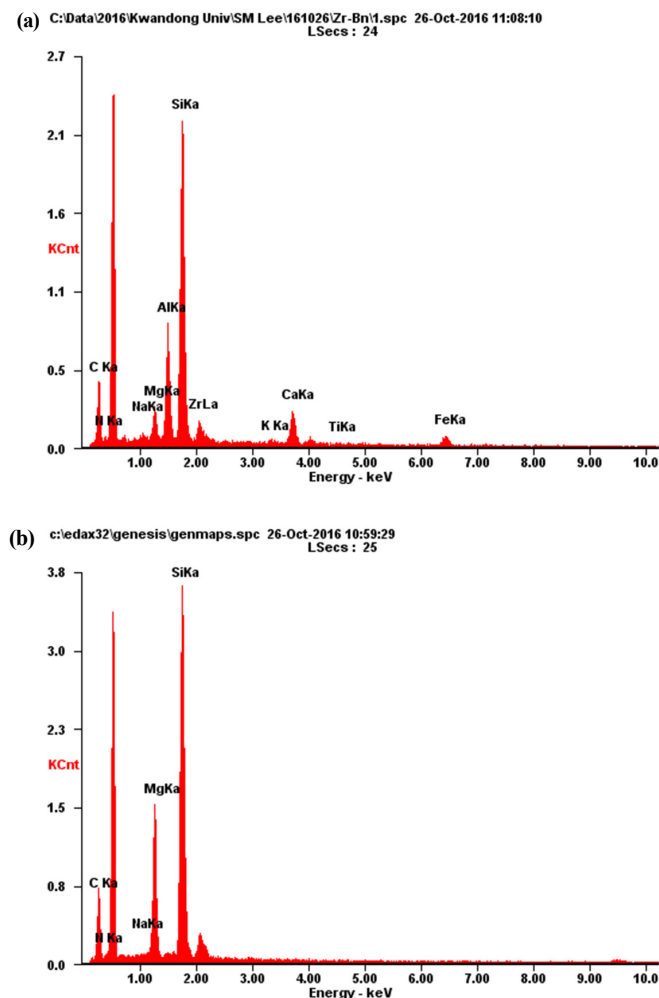


Figure 2. EDX graph of (a) Zr-Bentonite, and (b) Zr-Hectorite solids.

surface possessed a normal porous surface structure and the aggregated fine particles, probably Zr-particles, are seen at the surface. The Zr-bentonite showed layered structure and pores are evidently visible at the surface. The Zr-hectorite exposed porous structure with extra heterogeneity. Further, the EDX analytical spectra are given in Figure 2. The major elements in Zr-Bentonite are Si, and Al with smaller contents of Ca, K, Mg and Na. Moreover, the peak corresponding to Zr is clearly shown in the EDX graph, which inferred the successful intercalation of Zr into the clay structure. Similarly, the Zr-Hectorite showed Si and Mg as the main component with K and Na as a minor component.

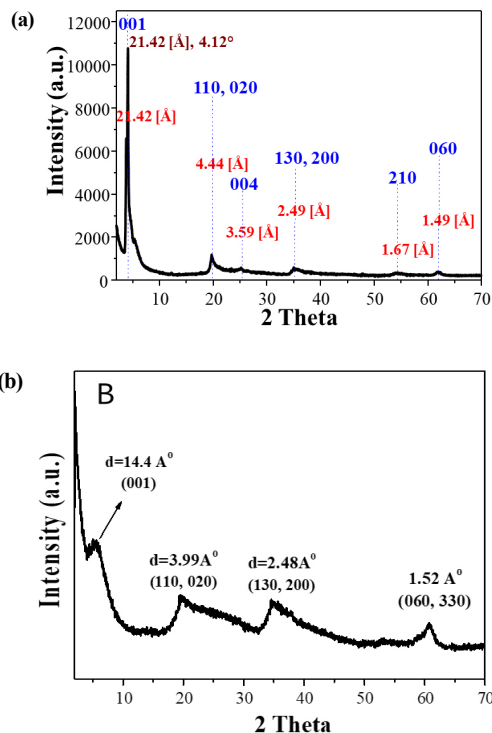


Figure 3. X-ray diffraction patterns of (a) Zr-Bentonite; and (b) Zr-Hectorite.

The data for the XRD pattern was collected for Zr-Bentonite and Zr-Hectorite and the plotted graphs are given in Figure 3. The XRD pattern of Zr-Hectorite resembles the XRD pattern of naturally occurring clay suggesting that the preparation of synthetic clay was successful. The diffraction peaks corresponding to 001 plane is obtained at 2 theta values of 4.12° and 6.6° with the d-spacings of 21.42 and 14.4 Å for Zr-Bentonite and Zr-Hectorite, respectively. As seen in the figure, the d-spacing obtained for other planes in Zr-Hectorite are similar or have proximity with the naturally occurring bentonite clay.

The surface functional groups present with the Zr-Bentonite and Zr-Hectorite are identified using FT-IR analysis (Figure 4). The main peak at 3435 cm^{-1} is due to the -OH stretching vibration[26]. A prominent peak at the wavenumbers around 1631 and 1422 cm^{-1} is attributable to symmetric and asymmetric stretching of the carboxyl group present in the material[27]. The vibrational peak appeared at 1008-1046 cm^{-1} is due to the asymmetric stretching vibrations of Si-O-Si[28], and the small peaks obtained at around 920 and 820-680 cm^{-1} are assigned to the Si-OH and Si-O-Si, respectively[29,30].

3.2. Batch removal of arsenic (V)

3.2.1. Effect of solution pH

The solution pH often influences the extent of adsorption since the pH of the solution alters the surface properties of the material and speciation of the pollutant molecules in solution[31]. The removal of arsenic (V) using Zr-Bentonite and Zr-Hectorite were studied at various initial pH of the solution; i.e., from pH 2.0 to 9.0. Fig. 5 showed that

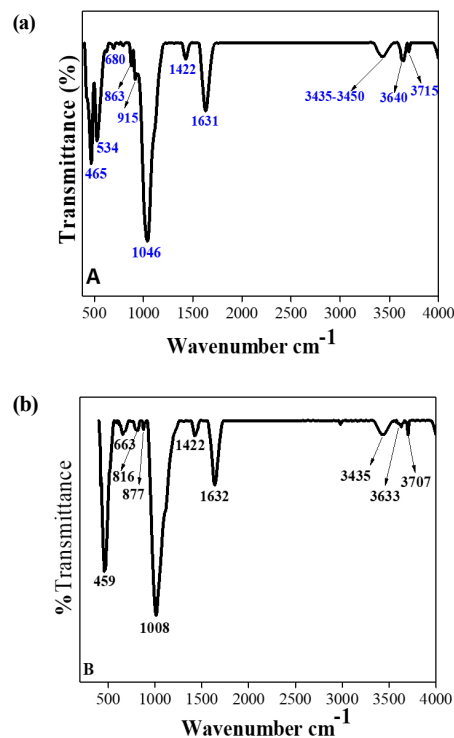


Figure 4. FT-IR Spectra of (a) Zr-Bentonite; and (b) Zr-Hectorite solids.

the percentage removal of arsenic (V) using Zr-Bentonite and Zr-Hectorite were relatively high at low pH 2.0 value. The removal efficiency of Zr-Bentonite remained almost constant up to pH 5.0, which slightly decreased with increasing the pH from 5.0 to 8.0. Further, there is an abrupt reduction of elimination efficiency of Zr-bentonite for arsenic (V) removal at pH > 8.0. On the other hand, the percentage removal of arsenic (V) using Zr-Hectorite rapidly decreased from 86.34 to 66.94% with an increase in pH from 2.0 to 3.0. Further, with an increase in pH from pH 3.0 to 9.0 the percentage removal of arsenic (V) was decreased gradually and only 26% of arsenic (V) was removed at pH 9.0. These results could be explained with the help of arsenic (V) speciation in aqueous media as well as the pH_{PZC} of the solid materials. The pH_{PZC} of Zr-Bentonite and Zr-Hectorite are found to be 8.0 and 4.5, respectively. The high percentage removal of arsenic (V) at lower pH region of 2.0 to 8.0 is attributable to electrostatic attraction between the positive charge on the surface of Zr-Bentonite and negatively charged arsenic (V) species[32]. However, $\text{pH} > 8.0$, the removal of arsenic (V) was decreased significantly due to the strong repulsive forces operative between the anionic species of arsenic (V) and the negatively charged surface of Zr-Bentonite. It was further assumed that the adsorption of arsenic (V) predominantly occurred through the active sites that created from the incorporated zirconium on the materials through the formation of Zr-O-As bonds[20,33,34]. Therefore, relatively less uptake of arsenic (V) by Zr-Hectorite is due to the smaller extent of zirconium loading within the synthetic clay network. In addition, the low uptake of arsenic (V) by Zr-Hectorite at higher pH is because of electrostatic repulsion between negatively charged surface of

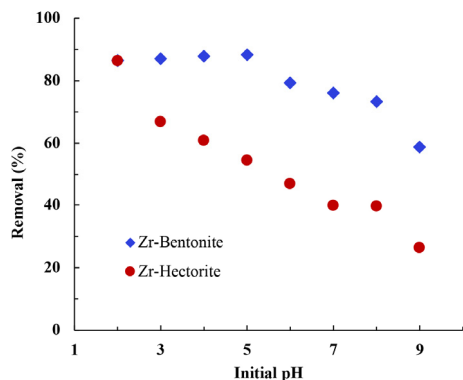


Figure 5. Effect of pH in the removal of arsenic (V) using Zr-Bentonite and Zr-Hectorite solids.

Zr-Hectorite and predominant anionic species of arsenic (V)[32]. Previously, the similar effect of solution pH on the removal of arsenic(V) was also obtained using iron-oxide modified sericite alginate beads[28], iron oxide modified clay-activated carbon composite beads [35] and zirconia nanoparticle-loaded hydrogel[17].

3.2.2. Effect of Initial arsenic (V) concentration

The effect of initial concentration of pollutant was carried out by varying the initial concentration between 2.0 and 26.0 mg/L at constant pH 5.0. The results are given in Figure 6. At lower concentration (i.e., 2 mg/L), the percentage removal of arsenic(V) using Zr-Bentonite and Zr-Hectorite were more than 90% and 80%, respectively. The percentage removal was decreases from 91.30 to 69.50% and 83.57 to 34.84% using Zr-bentonite and Zr-hectorite, respectively while the initial concentration of arsenic(V) increases from 2.0 and 26.0 mg/L. Further, the equilibrium sorption data obtained at various concentration of arsenic(V) were modelled with Freundlich and Langmuir adsorption isotherms using its linear form[36]. The graphs were plotted as $\log C_e$ vs $\log q_e$ and C_e/q_e vs C_e for the Freundlich and Langmuir adsorption isotherms, respectively. The values of Freundlich and Langmuir constants along with the R^2 values obtained are given in Table 1.

The R^2 values in Table 1 showed that the fitting equilibrium sorption data to the Freundlich adsorption isotherm is better fitted than the Langmuir adsorption model. The suitability of the Freundlich equation indicated that strong chemical forces were involved in the removal of arsenic (V) using Zr-Bentonite and Zr-Hectorite[36]. Moreover, the Langmuir monolayer capacity (q_0) and the Langmuir constants (K_L) were calculated and the relatively high values of Langmuir constant specify the affinity of these materials towards arsenic (V)[37]. The Langmuir monolayer sorption capacity obtained for Zr-Bentonite was significantly higher than that of Zr-Hectorite.

3.2.3. Effect of contact time

The effect of contact time on the removal of arsenic (V) using both Zr-Bentonite and Zr-Hectorite were conducted and the percentage of arsenic (V) removed at various contact times are shown in Figure 7. The initial uptake of arsenic (V) was relatively faster and Ca 44 and

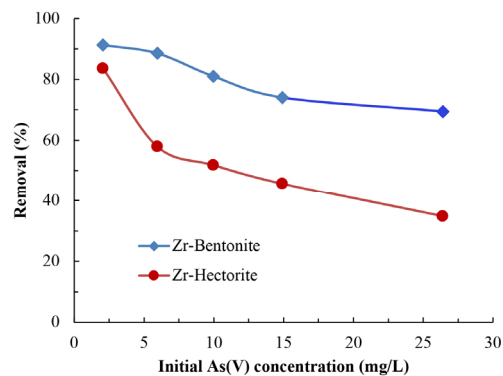


Figure 6. Effect of initial concentration in the removal of arsenic (V) using Zr-Bentonite and Zr-Hectorite solids.

Table 1. Langmuir and Freundlich Adsorption Isotherm Constants Obtained for Arsenic (V) Removal Using Zr-Bentonite and Zr-Hectorite Solids

	Langmuir isotherm			Freundlich isotherm		
	q_0 (mg/g)	K_L (L/g)	R^2	1/n	K_F (mg/g)	R^2
Zr-Bentonite	4.608	0.356	0.913	0.571	1.109	0.984
Zr-Hectorite	2.207	0.234	0.947	0.433	0.524	0.987

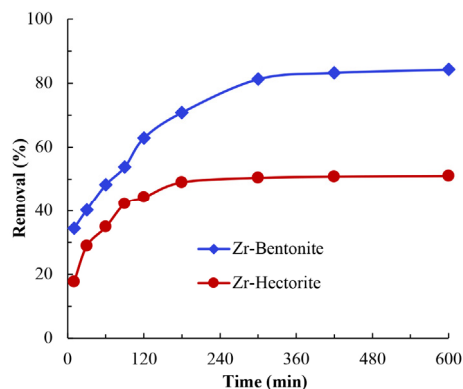


Figure 7. Effect of contact time in the removal of arsenic (V) using Zr-Bentonite and Zr-Hectorite solids.

62% of arsenic (V) was removed within 120 min of contact time. Further, the lapse of time (> 120 min), the uptake of arsenic (V) was slowed down and an apparent equilibrium was attained at 300 min of contact time. The time required to reach the sorption equilibrium in this study was similar or even faster than that of the equilibrium time reported for arsenic adsorption using clay and clay based materials [38,39].

Further, the pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models were utilized to study the adsorption kinetics of arsenic (V) using the Zr-Bentonite and Zr-Hectorite. The PFO and PSO equations were taken to its linear form[40]. The graphs were plotted between $\ln(q_e - q_t)$ vs t and t/q_t vs t for PFO (Figure 8(a)) and PSO models (Figure 8(b)), respectively. The rate constant (k_1 and k_2) and the up-

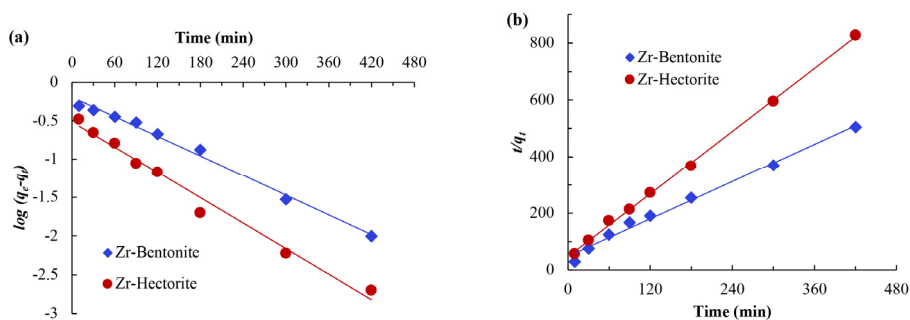


Figure 8. Plots of (a) PSO kinetic; and (b) PSO kinetic models for the sorption of arsenic (V) using Zr-Bentonite and Zr-Hectorite solids.

Table 2. Rate Constants (k_1 and k_2), Sorption Capacity (q_e) and R^2 Values Obtained from PFO and PSO Kinetic Models for the Sorption of Arsenic (V) Using Zr-Bentonite and Zr-Hectorite Solids

	Pseudo-first order kinetics			Pseudo-second order kinetics		
	k_1 (1/min)	q_e (mg/g)	R^2	k_2 (g/mg. min)	q_e (mg/g)	R^2
Zr-Bentonite	0.0043	1.209	0.992	0.025	0.911	0.990
Zr-Hectorite	0.0055	1.672	0.984	0.072	0.542	0.999

take capacity (q_e) were calculated and given in Table 2. The kinetic data collected agreed well to the PSO model since higher values of R^2 were obtained for both materials. The suitability of the PSO kinetic model suggested that the interaction occurring at the solid/solution interface was invariably with stronger chemical forces[41].

3.2.4. Effect of dose of the adsorbent

The sorption study was conducted varying the dose of the adsorbents (1.0 to 5.0 g/L) and the percentage uptake of arsenic (V) at various doses of the materials are given in Figure 9. The percentage removal of arsenic (V) using Zr-bentonite and Zr-hectorite increases continuously with an increase in solid dose of the material from 1.0 to 4.0 g/L. Further, there is a small upsurge in the percentage uptake while the dose is increased from 4.0 to 5.0 g/L. In this study, 5.0 g/L was chosen as an optimum dose of Zr-bentonite and Zr-hectorite for the removal of arsenic (V) from aqueous solutions.

3.2.5. Effect of background electrolytes

To study the nature of interaction between the arsenic (V) and the Zr-Bentonite and Zr-Hectorite solids, the adsorption study was conducted in which the NaCl was used as a background electrolyte in a sorptive solution. The concentration of NaCl was increased to 1000 times, i.e., from 0.001 to 1.0 mol/L. As shown in Figure 10, an increase in the concentration of background electrolytes did not caused significantly the percentage uptake of arsenic (V) by Zr-bentonite and Zr-hectorite solids. Briefly, the removal of arsenic (V) by Zr-bentonite and Zr-hectorite was decreased from 88 to 80% and 54 to 51% while increasing the background electrolyte concentrations from 0.001 to 1.0 mol/L (NaNO_3). Therefore, the results inferred that the Zr-bentonite and Zr-hectorite are selective towards the arsenic (V) and arsenic (V) was sorbed specifically at the solid surface[32,42]. This result further

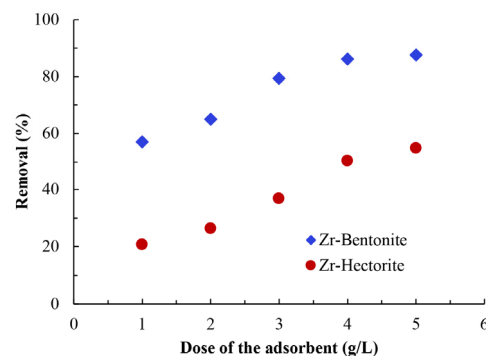


Figure 9. Effect of dose of the adsorbent in the removal of arsenic (V) using Zr-Bentonite and Zr-Hectorite solids.

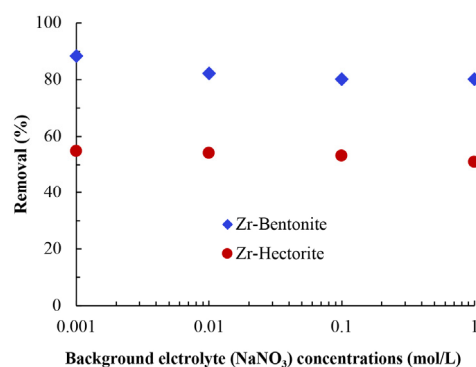


Figure 10. Effect of background electrolytes in the removal of arsenic (V) using Zr-Bentonite and Zr-Hectorite solids.

showed the potential applicability of Zr-loaded clay, i.e., Zr-Bentonite and Zr-Hectorite for the efficient removal of arsenic (V) from aquatic environments.

4. Conclusion

Zirconium was successfully intercalated within the natural bentonite clay and synthetic hectorite clay network. The materials are characterized by SEM-EDX, XRD, and FT-IR analyses. It has been observed that the structure of synthesized clay is similar to the structure of natural bentonite clay. The Zr-loaded clays were efficiently utilized for the removal of arsenic (V) in batch studies. Zr-Bentonite and Zr-Hectorite showed a high percentage removal of arsenic (V) within a wide range of pH and concentrations and the equilibrium state sorption data were fitted well to the Freundlich adsorption isotherm. The presence of background electrolytes in relatively high concentrations did not inhibit the uptake of arsenic (V), which suggested that the arsenic (V) was specifically sorbed at the solid surface. The study further showed that the natural bentonite clay incorporated with zirconium possessed relatively higher removal efficiency for arsenic (V) compared to the Zr-loaded synthetic hectorite clay. However, both the materials, i.e., Zr-Bentonite and Zr-Hectorite are having potential to be employed for the remediation of groundwater contaminated with arsenic (V).

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