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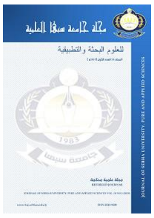

Adsorption of Chromium(VI) from an aqueous solution by the nano-zerovalent iron/activated sepiolite composite adsorbent

*Amal Juma Habish[a] , Asma M. Husin Milad[a], Feroz Jabir Mugber[b], Rada Petrović[c]

[a]Department of Chemical and Petroleum Engineering, Faculty of Engineering, Elmergib University, Alkhoms, Libya
[b]Department of Chemical Engineering, Faculty of Engineering, Tripoli University, Tripoli, Libya
[c]Faculty of Technology and Metallurgy, University of Belgrade, 11000 Belgrade, Serbia

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ABSTRACT

In this work, nano-zerovalent iron was deposited onto sepiolite (SEP) or acid-activated sepiolite (AAS) at different mass ratio in order to obtain efficient adsorbents for the removal of Cr(VI) from aqueous media. The composites were synthesized at support/nZVI ratios of 10:1, 5:1, 2.5:1 and 2:1. The removal of Cr(VI) was investigated at initial pH = 2. Through of the fabrication, the support suspension was ultrasound treated to deagglomerate it before nZVI deposition. Results of TEM analysis showed that better dispersibility of nZVI was achieved with SEP-based composites, but AAS-based composites had higher removal efficiency. Higher efficiency of Cr(VI) removal was achieved when the higher content of nZVI in the composites. AAS/nZVI Composite with the ration 2:1 provided the best removal of Cr(VI).

إمتزاز أيون الكروم من المحاليل المائية بإستخدام الحديد النانو صفري التكافؤ مع سيبيولايت المنشط بالحمض كمادة مركبة مازة

*أمال جمعة إحبيش[1] و أسماء مصطفى ميلاد[1] و فيروز جابر مجبر[2] و رادا بيتروفيتش[3]

[1]قسم الهندسة الكيميائية والنفطية، كلية الهندسة، جامعة المرقب، ليبيا
[2]قسم الهندسة الكيميائية، كلية الهندسة، جامعة طرابلس، ليبيا
[3] كلية التقنية والمعادن، جامعة بلغراد، بلغراد، صربيا

الملخص

في هذا العمل، تم ترسيب الحديد النانو الصفري التكافؤ (nZVI) على السيبيولايت (SEP) أو السيبوليت المنشط بالحمض (AAS) بنسب وزنية مختلفة من أجل الحصول على مواد مازة فعالة لإزالة Cr(VI) من الوسط المائي. تم تصنيع المواد المازة المركبة المدعومة ب nZVI عند نسب 10:1 ، 5:1 ،: 2.5 1 و 2:1. تم إختبار إزالة Cr (VI) عند الرقم الهيدروجيني الإبتدائي 2 = (pH) و 3. أثناء التحضير ، تمت معالجة معلق السيبولايت بالموجات فوق الصوتية وذلك لتفكيك التكتل قبل ترسب nZVI. أظهرت نتائج تحليل TEM أنه اقضل انتشار كان لـ nZVI في على حالة SEP بمفرده ، ولكن المواد المركبة من AAS / nZVI كان لها كفاءة إزالة أعلى. اعطت المواد المركبة المحتوية على نسبة عالية من nZVI كفاءة أعلى لإزالة أيون Cr(VI) كانت إزالة Cr(VI) أكثر كفاءة عند الأس الهيدروجيني الأبتدائي = 2 مما كانت عليه عند الرقم الهيدروجيني الأبتدائي = 3. قدم المركب AAS / nZVI مع نسبة 2: 1 أفضل إزالة لـ Cr (VI).

الكلمات المفتاحية:
الحديد النانو الصفري التكافؤ (nZVI)
السيبيولايت
التنشيط بالحمض
انتشار
ايون Cr(VI)
الامتزاز
مواد مركبة

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*Corresponding author:
E-mail addresses: amaljuma845@gmail.com, (A. M. H. Milad) asma.aga2009@gmail.com, (F. J. Mugber) rosemarry44@yahoo.com, (R. Petrović) radaab@tmf.bg.ac.rs

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Introduction

Towards increase concern about the global environmental pollution problem, almost the researchers have dedicated their efforts to find available approaches to deal with heavy metal ions. Metal ions are not degradable unlike the traditional organic pollutants. Most of them are highly toxic or carcinogenic and are accumulated in living organisms. Widely uses of Chromium (Cr) is common in the most of industries namely; metallurgy, electroplating, printing, textile dyeing, and paper-making. Furthermore, bad disposal and controlling of Cr-rich residue and wastewater from production activities can lead to Cr being released into the environment, which causing observable harm to the water and soil environment and further affecting the ecosystem [1-3]. Several works have been conducted to remove Cr from waste water and soil [4-6]. As well, Singh et al. (2012) remediated Cr(VI) contaminated soil using nano-zerovalent iron (nZVI) with strong reduction ability [7]. The adsorption as one of the physical methods is commonly used to get rid of the contaminates due to its simple route, strong effects, less secondary pollution, and the potential of regeneration or reuse [8]. As well, the remediation of Cr-contaminated water and soil mainly immobilizes metal ions (i.e. Cr(VI)) by adsorption onto the surface or between the layers of an adsorbent [9], [10].

On the other hand, the removal performance of nZVI particles is relatively small due to its aggregation and oxidation in normal conditions, which decrease their reactivity by reduction specific surface area and producing a less negative oxidation–reduction potential. To resolve these problems, various stabilization methods have already been developed to facilitate the usage of nZVI in a varied range of environmental remediation scenarios. Recently, research interest has increased with regards to the use of porous materials including carbon materials, resins, and different natural minerals, such as montmorillonite, bentonite, kaolinite and sepiolite, have been applied for the support of nZVI particles with nZVI for the purifying of the aqueous solutions from Cr(VI) [11-15].

Sepiolite (hydrated magnesium silicate clay mineral, $Mg_8Si_{12}O_{30}(OH)_4(OH_2)_4{\cdot}8H_2O$) was applied as a support material, to improve stability of nZVI particles and to provide high surface area to interact with Cr(VI). Furthermore, nZVI was strongly incorporated onto an acid activated sepiolite and the resulted composite was shown a significant influence to remove the Cr(VI) ions from water than the pure nZVI [14]. However, there has been no systematic study of the effect of acid-activation of the sepiolite or some other synthesis factors on the removal efficiency of the nZVI/sepiolite composites for Cr(VI) removal.

In this study, the efficient removal of Cr(VI)) from aqueous solution by support/nZVI at different mass ratios (10: 1, 5:1, 2.5:1 and 2:1) was examined at initial pH 2.0 ± 0.1 . The sepiolite (SEP) and acid-activated sepiolite (AAS) as supports were used. The purpose of this work was to obtain the optimal ratio support/nZVI for the removal efficiency of Cr(VI)from aqueous solutions and to investigated the influence of pH value on the adsorption capacity.

Experimental work

1. Materials and chemicals

A fraction < 250 μm of natural sepiolite (SEP) from Andrići (Serbia), was used in the experiments. All chemical reagents used in this study, $FeSO_4{\cdot}7H_2O$, $NaBH_4$, absolute ethanol, HNO_3, NaCl, HCl, NaOH, and $K_2Cr_2O_7$ were of analytical grade. The solutions was prepared by dissolving $K_2Cr_2O_7$ in demineralized water (Millipore Milli-Q 18 MΩ).

2. Synthesis of nZVI and supported/nZVI samples

The support/nZVI samples were performed using the traditional chemical reduction procedure [16]. A suspension of 5 g of SEP or AAS in 500 cm^3 of ethanol/water solution mixture (1:4 v/v) was first ultra-sonicated for 10 min, using a Sonics ultrasonic processor of 750W output with a 20 kHz converter and a solid titanium probe of 19 mm diameter to provide de-aggregation of the SEP/AAS [17].

The suspension pH was adjusted to 4 by adding drops of 0.1 mol/dm^3 HNO_3 solution. Then, $FeSO_4{\cdot}7H_2O$ was added in the quantity to achieve the support/nZVI rations of 10:1, 5:1, 2.5:1 or 2:1 (2.5, 5.0, 10.0 or 12.5 g respectively).

The ultrasonic treatment was repeated for a further 10 min. The suspension was transferred to a flask and stirred for 30 min under a nitrogen flow, followed by the dropwise addition of 100 cm^3 of a freshly prepared $NaBH_4$ solution of concentration 0.5 or 1.0 or 2.0 or 2.5 mol/dm^3, respectively, depending on the quantity of $FeSO_4{\cdot}7H_2O$. For example, for the sample with the support/nZVI rations of 10:1, mass of $FeSO_4{\cdot}7H_2O$ was 2.5 g, and the concentration of $NaBH_4$ solution was 0.5 mol/dm^3.

Molar ratio $NaBH_4$:Fe^{2+} was approximately 5:1, which is lots more than the stoichiometric ratio. In that way, the reaction will be faster and the nZVI particles will be deposited uniformly. The suspension was left in the flask with stirring under the N_2 atmosphere for 15 min. The solid material was separated from the other phase via vacuum filtration, washed many times with pure ethanol, under a N_2 atmosphere, and dried under vacuum for 12 h at 60 °C [17].

3. Characterization of SEP/AAS-nZVI (2.5:1)

The transmission electron micrograph (TEM) analysis of samples with the support/nZVI ratio 2.5:1 was performed on a JEOL T-100 instrument. The samples were prepared by grinding and subsequent dispersing of the powder using ultrasonic technique in ethanol. A drop of the dilute suspension was applied on carbon-coated grids.

4. Adsorption Experiments

The adsorption experiments were investigated by a batch method. The adsorbents and ion solutions were equilibrated in a thermostated water bath with shaker. The initial solution pH was adjusted by using HNO_3 or KOH solutions. The adsorption of Cr(VI) ions was investigated at pH 2.0 ± 0.1. After equilibration, the adsorbents were separated from the solutions and the solutions pH were measured by using a pH meter (Ino Lab WTW series pH 720).

The initial and final concentrations of Cr(VI) ions were measured through using atomic absorption spectrometer (AAS) (Perkin Elmer 730). All the experiments were performed double, and results were given as the average of two measurements [17].

The adsorbed per adsorbent at equilibrium, q_e (mg/g), was calculated according to equation [18]:

$$q_e = \frac{C_i - C_e}{m} V \qquad (1)$$

where: C_i and C_e are the initial and the equilibrium concentrations (mg/dm^3), m is the mass of an adsorbent (g), and V is the volume of a solution (dm^3).

The Cr(VI) adsorption was performed at varioust initial concentrations with the goal of determine adsorption isotherms and compare the maximal adsorption capacities of the composite synthesized with different ration SEP/AAS-nZVI, at initial pH 2.0 ± 0.1.

Results and discussion

1. TEM analysis

TEM of the SEP-nZVI(2.5:1) and AAS-nZVI(2.5:1) composites (Fig. 1) show that the sepiolite particles provided much better dispersibility of nZVI (Fig. 1a) than acid-activated sepiolite, where the nZVI particles were highly aggregated (Fig. 1b), mostly apart from the sepiolite particles.

The nZVI particles in SEP-nZVI(2.5:1) were spherical and smaller than 100 nm. Better dispersibility of AAS-based samples was previously confirmed by SEM analysis of all samples [17].

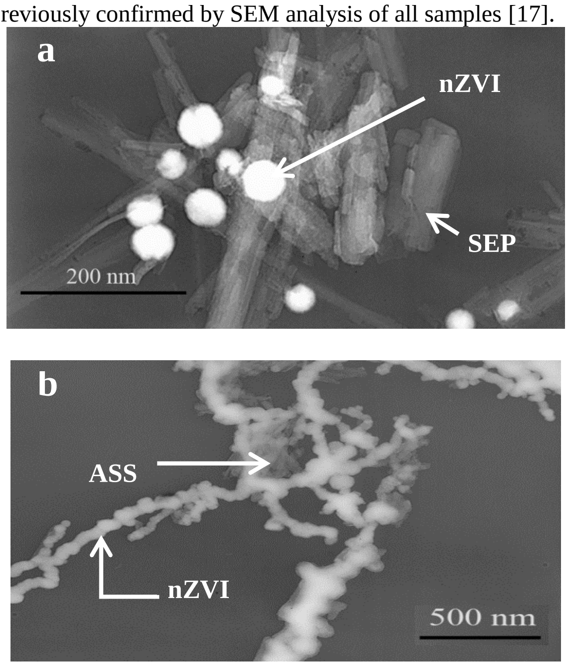
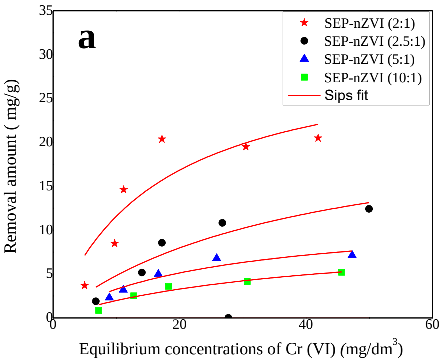


Figure 1: Transmission Electron Micrographs (TEM) of the (a) SEP-nZVI(2.5:1) and (b) AAS-nZVI(2.5:1) composites.

2. Adsorption of Cr(VI) onto the nano-zerovalent iron/activated sepiolite composite

The Cr(IV) adsorption was investigated at initial pH 2.0 ± 0.1 from different initial concentrations in order determine the adsorption isotherms for the composites and compare their maximal adsorption capacity. Taking into concern the foregoing analysis and the fact that the commercial method for the removal of Cr(VI) from water is its reduction in acid conditions and $Cr(OH)_3$ precipitation in basic conditions [12], the Cr(VI) adsorption onto nZVI composites was analyzed in this study in acid conditions, at initial pH 2.0 ± 0.1. The dependences of the adsorbed amount of Cr(VI), q_e, on the Cr(VI) equilibrium concentration, (C_e), are presented in Fig. 2.



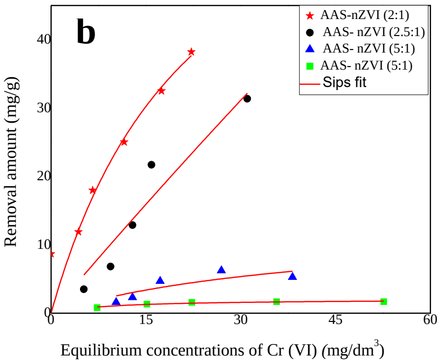


Figure 2: Adsorption isotherm for Cr(VI) ions onto SEP-nZVI (a) and b)AAS-nZVI composites at pH_i = 2.0 ± 0.1.

As seen from Figs. 2, the adsorption capacity increased as the quantity of nZVI in the composite increased. Based to the literature [19], the adsorption of the Cr(VI) anions only on the sepiolite or acid-activated sepiolite were negligible, even at low initial pH values, due to negatively charged surfaces for wide range of pH values [19]. Therefore, the content of nZVI was the issue that determined the adsorption capacity of the composites.

The adsorption capacities of AAS–nZVI composites were higher than of SEP-nZVI, despite the fact that the nZVI particles were better dispersed on the surface of SEP. The reason could be the higher oxidation of SEP–nZVI during the synthesis, as was shown in previous work [17]. The highest adsorption capacity was achieved with the AAS/nZVI composite with the ration 2:1, at initial pH=2.

The dependences of the final solution pH value (pH_{final}) after equilibration of Cr(VI) solutions with SEP-nZVI and AAS-nZVI samples on the different initial concentrations of the Cr(VI) solution are presented in Fig. 3. the pH value of aqueous media is an important parameter that influences the adsorption process; it determines both the surface charge of the adsorbent and the existing form of Cr(VI)).

According to Fig. 3, the equilibrium pH values stabilized as the initial concentration of the Cr(VI) solution increased from 2.5 to 3 for SEP-nZVI and AAS-nZVI samples at an initial pH of 2.0. Due to the highly acidic conditions in the suspensions of both SEP/AAS-nZVI samples, a significant increase in the final pH value was not observed at an initial pH value of 2.0. Besides, the final pH decreased as the Cr(VI) concentration increased. Namely, pH decreased with the Cr(VI) concentration increasing, indicating higher releasing of H^+ ions into the solution than the consumption/binding of the ions to the surface, i.e., higher consumption of OH^- ions. This H^+ is releasing or OH^- consumption suggests specific adsorption of Cr^{3+} ions (inner-sphere complexes) or formation of $Cr(OH)_3$ and $Fe(OH)_3$.

Regardless of different forms, Cr(VI) is always present as anion: $HCrO_4^-$ is the main species at low concentrations at pH roughly 2–4, CrO_4^{2-} becomes the dominant species at pH ≥ 7, whereas $Cr_2O_7^{2-}$ and $HCrO_7^{2-}$ exist only in solutions of high concentration. It was shown that the removal of Cr(VI) by various adsorbents is extremely dependent on the solution pH [14, 15],[19-22].

Generally, the efficiency of the Cr(VI) amount decreases as pH increases. One of the reasons is the increase of negative charge on the adsorbent surface [20] and, thus, stronger repulsive forces between Cr(VI) anions and negatively charged surface. More H^+ ions are existed in the solution as the pH value decreases. The protonation degree of the functional groups on the adsorbent surface increases (i.e., Si-OH or Al-OH functional groups), which is promising for the adsorption of negatively charged ions. Furthermore, the acid condition favors the reduction of Cr(VI) to Cr(III) by nZVI using the following chemical equation:

$$CrO_7^{2-} + 2Fe + 14H^+ \rightarrow 2Cr^{3+} + 2Fe^{3+} + 7H_2O \qquad (2)$$

It is believed that the removal of Cr(VI) involves instantaneous adsorption of Cr(VI) on the nZVI surface, where the electron transfer takes place. Cr(VI) is reduced to Cr^{3+} during the oxidation of nZVI to Fe^{3+}, resulting in the precipitation of mixed Cr and Fe hydroxides [23]. When the pH values were high, Cr(III) and Fe(III) hydroxides are undoubtedly developed, forming a passivation layer that hindered Cr(VI) access to the nZVI surface and inhibited further decomposition of surface iron.

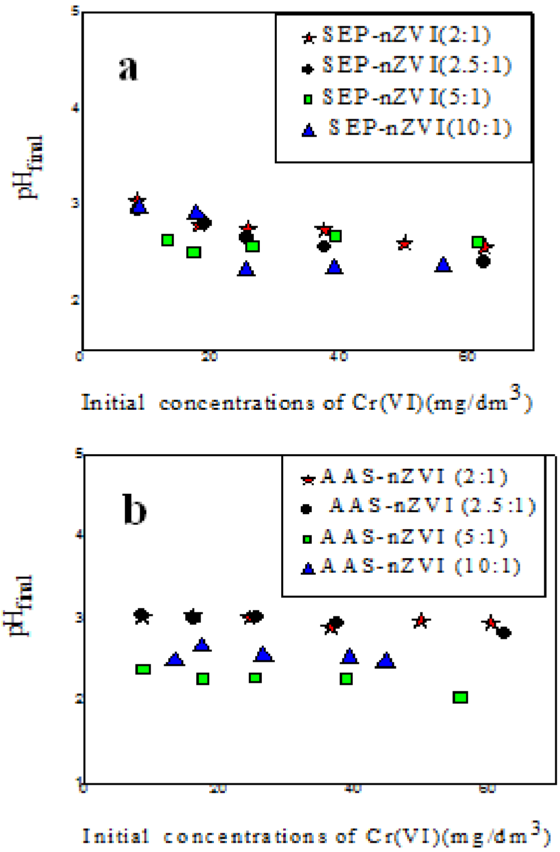


Figure 3: Dependences of the final solution pH value on the different initial Cr(VI) concentration of SEP-nZVI (a) and AAS-nZVI (b) composites at initial pH values 2.0 ± 0.1.

In contrast, a lower pH values, the higher concentration of H^+ causes corrosion of nZVI particles by reason of the reaction of nZVI with dissolved oxygen and water molecules. This would renew the fresh reactive sites and improving electron transfer from nZVI to Cr(VI), resulting in a considerable increase in Cr(VI) to Cr(III) reduction [24]. It should be stated that, while lower pH values could regenerate the reactive sites on nZVI particles, this would also reduce the lifespan of nZVI particles over time.

2.1. Equilibrium data modeling

The adsorption isotherms provides important data for understanding the mechanism of adsorption process (adsorbate-adsorbent interaction) as well as to estimate the maximum capacity of an adsorbent. Langmuir (Eq. (3)), Freundlich(Eq. (4)) and Sips(Eq. (5)) isotherm models has been selected to analyse the obtained experimental data, as following [25, 26]:

$$q_e = \frac{q_m K_L c_e}{1+K_L c_e} \qquad (3)$$

$$q_e = K_f c_e^{\frac{1}{n}} \qquad (4)$$

$$q_e = \frac{q_m K_s (c_e)^{n_s}}{1+K_s (c_e)^{n_s}} \qquad (5)$$

where: q_m is the maximum adsorption capacity (mg/g), K_L is the Langmuir constant associated with the energy of adsorption (dm^3/mg), K_f is the Freundlich constant associated with the adsorption capacity ($mg^{(1-1/n)}$ $dm^{3/n}/g$), n is the dimensionless sorption intensity parameter, K_a is the Sips equilibrium constant ($(dm^3/mg)^{n_S}$) and n_S is the index of heterogeneity.

The values of Freundlich , Langmuir and sips isotherm parameters are presented in Table 1 for the samples with high adsorption capacity. The Sips isotherm model best described the equilibrium data when the correlation coefficients were compared. A combined form of Langmuir and Freundlich models, the Sips isotherm [27], deduced for predicting the heterogeneous adsorption systems [28] and avoiding the limitation of the increasing adsorbate concentration related with the Freundlich model. The Sips model reduces to the Freundlich isotherm when the adsorbate content is much lower than the adsorbent capacity at low concentrations.

Table 1: Langmuir, Freundlich and Sips isotherms constants for the adsorption of Cr(VI) onto the composites of SEP and AAS with two different ratio and at $pH_i = 2.0 \pm 0.1$

		SEP-nZVI(2.5:1)	**SEP-nZVI(2:1)**	**AAS-nZVI(2.5:1)**	**AAS-nZVI(2:1)**
Langmuir model	K_L	0.026	0.061	0.002	0.043
	q_m	23.1	30.8	63.5	77.3
	R^2	0.859	0.748	0.897	0.857
Freundlich model	K_f	1.16	3.65	1.00	4.86
	1/n	0.63	0.49	1.01	0.67
	R^2	0.790	0.645	0.897	0.857
Sips model	q_m	13.0	23.8	44.0	53.9
	Ka	0.076	0.013	0.017	0.032
	n_S	2.66	3.94	3.28	0.833
	R^2	0.956	0.901	0.962	0.811

2.2 Comparison of Cr(VI) removal of our SEP/AAS-nZVI and nZVI based materials.

The contribution of our work was focused on the influences of mass ratio for SEP/AAS-nZVI at the optimum pH (about 2) on the Cr (VI) removal percentage. The most of previous papers were fixed the mass ratio of SEP/AAS-nZVI and studied the removal percentage at high values of pH [12, 14, 29, 30].

Based on our previous work [17] for Cd^{2+} removal, the composites synthesized at different support/nZVI ratios in order to achieve the best nZVI dispersibility and the highest adsorption capacity for Cd^{2+} ions. In addition, the results showed that the prevention of both aggregation and oxidation during the synthesis were necessary in order to obtain the SEP/AAS–nZVI composite with a high adsorption capacity.

Table 2: The previous researchers based on different materials supported nZVI particles

Adsorbent	Optimum pH	Adsorption capacity (mg/g)	Optimum mass ratio based materials: nZVI	Isotherm model	Ref
Bentonite-supported nZVI	4.5	42.08	1:1	Langmuir isotherm	[30]
Bentonite-supported nZVI	5.0	60.56	1:1	Langmuir isotherm	[12]
Montmorillonite-supported nZVI	3.0	19	na	na	[29]
Sepiolite-supported nZVI	6.0	43.86	9:1	Langmuir isotherm	[14]
Sepiolite or acid-activated sepiolite supported nZVI	2.0	23.8/53.9	2:1	Sips isotherm	This study

na: not available.

Furthermore, a brief summary of similar works using supported-nZVI particles and our work are presented in Table 2. The important parameters as pH, mass ratio and the resulted adsorption capacity. It could be concluded that our nano-composite (SEP/AAS-nZVI) provided good Cr(VI) removal capacity with low pH and mass ratio .

Last, based on our knowledge, the most of previous composite materials, such as bentonite [12, 30], montmorillonite [29] and natural Sepiolite [14] were used as support material for nZVI to remove Cr(VI), but till now, no report was used acid activated sepiolite as the support nZVI with different mass ratio and at low pH. The good dispersibility with low aggregation of the nZVI particles was achieved with mass ratio of 2:1, that increased the Cr(VI) removal from its aqueous solutions.

Conclusions

In this investigation, nano-zerovalent iron (nZVI) particles were deposited via chemical reduction onto natural (SEP) and partially acid-activated (AAS) sepiolite at various support/nZVI mass ratios (10:1, 5:1, 2.5:1, and 2:1) in order to get composites with good nZVI dispersibility and high efficiency for the removal of Cr(VI) from water. Morphology analysis by using scanning transmission electron microscopy (SEM) confirmed previous results that better dispersibility was achieved in SEP/nZVI than AAS/nZVI composites. The content of nZVI in the composites was a determining factor for the efficiency of Cr(VI) removal from water as the capability of support was negligible: the composites with low quantity of nZVI had very low removal capacity. Despite the better nZVI dispersibility in SEP/nZVI composites, the adsorption capacities of AAS–nZVI composites were higher. The equilibrium data was best described by the Sips isotherm model. The suggested mechanisms for Cr (VI) removal by the composites include Cr (VI) reduction to Cr (III), followed by Cr(III) adsorption of $Cr(OH)_3$ and $Fe\ (OH)_3$ co-precipitation, and electrostatic attraction between Cr(VI) and protonated functional groups of the composite.

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