EQUILIBRIUM AND KINETIC STUDY ON HEXAVALENT CHROMIUM SORPTION ON BENTONITE SUPPORTED ZERO VALENT IRON

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ABSTRACT

The potential application of bentonite supported zero valent iron as a sorbent is evaluated in this study. It overcomes the disadvantages of the zero valent iron referring to its tendency of easy agglomeration and oxidation. The removal efficiency in respect to chromium (VI) species and the corresponding sorption mechanism is investigated. The maximum removal efficiency amounts to 99.85 % at an optimal solution pH of 4.5, an initial concentration of 50 mg L$^{-1}$ and a sorbent dosage of 0.3 g at an ambient temperature. It is shown that bentonite supported zero valent iron can be successfully used to remove chromium (VI) ions from aqueous media. Freundlich and Langmuir sorption isotherm models are applied. The latter provides better description showing that chemisorption of chromium (VI) species proceeds leading to a uniform monolayer formation. According to the mechanism advanced a mixed hydroxide containing chromium (III) and iron (III) ions is formed on the bentonite supported zero valent iron surface. This is in an accord with the obtained pseudo second order kinetics model.

Keywords: sorption, bentonite, zero valent iron, chromium (VI) ion.

INTRODUCTION

Since ancient times Mongolians have a nomadic life. It requires breeding livestock. The livestock census of 2014 showed that the total number of livestock reached 52 million heads [1]. 10.9 million pieces of hides and skins were treated in Mongolian livestock sector by 2013. Leather products were manufactured for the domestic and world market. As of today, there are more than 34 leather and 100 leather garment businesses in Mongolia [2]. The leather tanning which is an important technological stage in leather industry converts the raw hides and skins into leather which is more durable and less susceptible to decomposition. Chromium (III) salts are used as tanning agents. During the tanning process chromium (III) species are transformed into chromium (VI) one. The latter are often present in industrial wastewaters in quantities exceeding the permissible limit. These wastewaters are treated in a central wastewater treatment plant. However, chromium (VI) ions leak directly into the environment without complete remediation because of the low capacity of the treatment plant. For this reason, chromium (VI) which is highly toxic, mutagenic, bio-accumulating and carcinogenic to humans contaminates significantly the environment.

Among the physical, chemical and biological methods for Cr (VI) species removal from aqueous media, the sorption is known for its simplicity and cost effectiveness. In recent years, studies on the removal of Cr (VI) from aqueous media have been conducted by batch sorption techniques using natural sorbents including Swietenia mahagoni shell [3], modified corn stalk [4], biochar [5], bone char [6], bentonite [7-10], zeolite [11] and synthetic sorbents such as metal organic framework based on copper-benzencarboxylates [12], mesoporous carbon microspheres [13], nano α-Fe$_2$O$_3$ [14], activated carbon [15], Mn$_3$O$_4$ nanomaterial [16], zeolite-polymer composite [17] and zero valent
iron [18,19]. The zero valent iron is one of these effective sorbents. It is known for its high surface energy and reactivity [20] and the greater number of reactive surface sites [21] due to its high specific surface area. Therefore, zero valent iron has been studied for the removal of a wide variety of organic pollutants including azo dye acid black 24 [22], reactive blue 50 [23], phenol, dyes, chlorinated organic compounds and nitro aromatic compounds [24] as well as inorganic pollutants including chromium (VI) [19, 25], phosphate ion [26], nitrate ion [24, 27], heavy metals such as cadmium, chromium, lead and arsenic ions [18, 24, 27, 28].

But the removal efficiency decreases due to agglomeration and oxidation of zero valent iron during the removal process which results in the formation of an oxide layer on its surface [29]. Many researchers mention that there are further technical challenges related to the low stability and the difficult separation from the treated solution [24]. To address these issues, some porous materials including bentonite [30 - 35], montmorillonite [36 - 38], chitosan [39], kaolinite [40], zeolite [38, 41], activated carbon [42], sepiolite [43, 44], mesoporous silica [45], multiwalled carbon nanotubes [29], resin [46] and SBA-15 [20] are applied to support zero valent iron.

Mongolia is rich in mineral resources such as zeolite, bentonite and kaolinite, etc. Over 6000 deposits of 80 different minerals have been discovered. Even though about 10 deposits of bentonite are known, they are almost not used for specific purposes. Thus, it is possible to develop a supporting material for zero valent iron on the ground of this raw material, which is low cost and abundant.

The possible application of bentonite from Zagiin Oi deposit, Mongolia, as a supporting material of zero valent iron is evaluated in the present study. The sorption capability of the sorbent prepared in respect to chromium (VI) ions and the optimal conditions of sorption in a batch system are determined. The sorption data are analyzed using sorption isotherm and kinetic models.

**EXPERIMENTAL**

**Preparation of the sorbent**

The mineralogical composition of the bentonite used as a supporting material referred to 57.9 % of quartz, 19.3 % of albite, 11.6 % of muscovite and 11.2 % of anorthite. The mixture of the bentonite and the zero valent iron (B-ZVI) of a theoretical mass ratio of 1:1 was prepared using the wet chemical method described in refs. [23, 31, 35]. 9.660 g iron chloride were dissolved in 50 ml of a mixture of water and ethanol of a volume ratio of 1:4. Then 2.000 g of bentonite were added into the iron chloride solution, the mixture was stirred for 10 min. Then 0.93 mol L⁻¹ borohydride solution was added drop by drop with vigorous stirring. The mixture was continuously stirred for 20 min aiming a complete reduction. The synthesized solid particles were washed with ethanol (99.7 %) three times to remove residual water and conditioned at 338 K. The iron particles were stored under ethanol at 277 -278 K.

**Characterization of the sorbent**

The specific surface area of bentonite, zero valent iron and B-ZVI was determined using the single point Brunauer-Emmet-Teller (BET) technique. The calculation was done on the ground of the first part of N₂ sorption isotherm which was obtained at liquid nitrogen temperature in a surface area analyzer (Flowsorb III 2305 - 2310, USA). The X-ray diffraction (XRD) patterns of bentonite and B-ZVI were collected on an X-ray diffractometer (Shimadzu, MAXima_X XRD-7000, Japan) using Cu Kα radiation under normal atmospheric conditions. The data were recorded in the 20 range of 14 - 80° in steps of 0.05° with a scan speed of 8 °min⁻¹.

**Determination of chromium (VI) concentration**

The concentration of chromium (VI) ion was determined with conventional spectrophotometric methods using the coloured complex of 1,5-diphenylcarbazide with Cr (VI) ions [47]. 0.2 mL of concentrated phosphoric acid, appropriate amounts of chromium (VI) ions of a final concentration in the range of 10 mg L⁻¹ - 80 mg L⁻¹ and 2.0 mL 1,5 - diphenylcarbazide solution (0.1 %) in ethanol were added in a 25 mL volumetric flask. After that the solution was left at room temperature for 15 min. Then a portion of it was transferred to a glass cell, and the absorbance spectra in the visible light range was scanned against distilled water as a reference using UV-Vis spectrophotometer (Cary 60, USA).

**Sorption studies**

A portion of a mixture containing 0.30 g B-ZVI and 200 mL chromium (VI) solution (C₀ = 50 mg L⁻¹ pH = 4.5) was transferred to 250 mL flask at 300 K. The mixture were continuously stirred within 100 min with a constant
speed aiming to achieve an equilibrium. The pH value of 4.50 was kept constant during the adsorption experiments.

Different experimental parameters such as sorbent dosage, initial pH and chromium (VI) concentration were optimized to obtain maximum removal efficiency of chromium (VI) ions using B-ZVI of a mass ratio of 1:1. The initial concentration of chromium (VI) ions, the sorbent mass and the pH value were optimized by varying in the ranges of 50 - 200 mg L\(^{-1}\), 0.10 g - 0.50 g and 2 - 10, correspondingly.

The pH was adjusted with 1.0 M NaOH or 1.0 M HCl solutions. The solution pH and the oxidation/reduction potential (ORP) in the course of the batch experiments were measured with a pH/ORP meter (HI 2211, USA). Prior to each analysis the solution samples were filtered through a filter paper (Ø 45 μm) using the vacuum filtration technique.

The sorption capacity, \( q \), mg g\(^{-1}\), was calculated on the ground of the following equation:

\[
q = \frac{(C_0 - C)V}{W}
\]

where \( C_0 \) and \( C \) were the initial and current chromium (VI) ions concentrations, mg L\(^{-1}\), respectively, \( V \) was the volume of the chromium (VI) ions solution, L, while \( W \) was the sorbent weight, g.

RESULTS AND DISCUSSION

Determination of the mass ratio of bentonite and zero valent iron

Characterization of the sorbent

Fig. 1 shows the XRD patterns of ZVI and B-ZVI under ambient conditions. The characteristic broad peak at 20 of 45° indicates that the amorphous zero valent iron is predominantly present in the sample, while the observed broad reflection at around 2.02 Å is characteristic for ZVI at Fe 110 plane [48]. Bentonite supported ZVI is a mixture as the characteristic peaks of bentonite and ZVI appear independently from each other.

The specific surface areas are determined on the basis of the BET method. They are found equal to 14.42 m\(^2\) g\(^{-1}\), 117.07 m\(^2\) g\(^{-1}\) and 65.71 m\(^2\) g\(^{-1}\), respectively. The specific area of B-ZVI coincides approximately with the mean geometric areas of bentonite and ZVI indicating that that no surface process is involved in the mixture formation. This pattern is preserved with the mixture of ZVI and bentonite mass ratio of 1:2 and 1:4. The oxidizing rate is relatively low in case of B-ZVI compared with that in ZVI indicating stability increase.

Comparison of the removal efficiency of sorbents of a different mass ratio

The removal efficiency of several types of sorbents is compared. The experiments are conducted within 60 min using natural bentonite, zero valent iron and bentonite supported zero valent iron. The results are illustrated by Fig. 2.

As seen from Fig. 2, bentonite supported zero valent iron removes 100 % chromium (VI) ions from the solution, while that of bentonite and zero valent iron amounts to 4.55 % and 94.81 %, correspondingly. Apparently, almost no sorption occurs on bentonite surface.
Moreover, bentonite supported zero valent iron can be treated as a more effective sorbent than zero valent iron because of its higher sorption capacity. It is suggested that bentonite hinders the association of zero valent iron particles and decreases zero valent iron drawbacks such as its easy oxidation in an aqueous solution and surface activity loss due to agglomeration. Hence, bentonite which is widespread in nature, low-cost and not applicable for specific purposes can be used as a supporting material of zero valent iron.

Taking this into consideration, it is important to determine the optimal mass ratio of bentonite to zero valent iron in the mixture. Adsorption experiments are carried out within 100 min using mixtures of bentonite to ZVI ratios of 4:1, 2:1 and 1:1. The results obtained are compared in Fig. 3.

It is evident from Fig. 3 that the removal efficiency increases from 54.11 % to 100 % while the ratios studied change from 4:1 to 1:1. It is clearly seen that the removal efficiency in respect to chromium (VI) ion and mass of zero valent iron in the mixture are directly proportional; on the other hand, sorption can occur on zero valent iron surface which acts as a sorbent. Hence, the optimal mass ratio chosen refers to 1:1 (B:ZVI).

**Optimal condition determination**

**Effect of the operating time**

The effect of the operating time is examined by its variation in the range of 5 min-60 min at pH = 4.5. Fig. 4 shows the relation between the sorption capacity in respect to chromium (VI) ions and the operating time.

The maximum sorption capacity is 42.08 mg g⁻¹ in case of 60 min sorption. The sorption capacity increases rapidly during the first ten minutes because a large number of binding sites are available at the beginning of the process.

The adsorption capacity increases gradually with the further time increase because the number of binding sites decreases and the remaining sites are difficult to occupy. An equilibrium is attained within 40 min - 50 min.

**Effect of B-ZVI dosage**

The removal efficiency in respect to Cr (VI) ions as a function of B-ZVI dosage is investigated within 50 min varying the latter from 0.1 g and 0.5 g. The results are illustrated in Fig. 5.

The removal efficiency increases from 37.85 % to 98.53 % with increasing B-ZVI dosage from 0.1 g to 0.3 g. In this case, the binding sites are completely saturated because the sorption capacity reaches its maximum value. The further increase of the adsorbent dosage results in removal efficiency increase. However, the binding sites are still unsaturated because they increase with adsorbent dosage increase. The value of the inflection point corresponding to the start of sorption capacity decrease provides to determine that the optimal dosage refers to 0.3 g.

**Effect of initial pH**

The existing chromium species in the aqueous solution depend on its pH. The effect of the solution initial pH on the removal efficiency is examined. The results
The removal efficiency decreases from 100 % to 34.94 % with pH increase from of 2.0 to 12.0. It is the highest in the range from 2.0 to 4.5 and starts to decrease at pH of 4.5. The rapid change of the removal efficiency shows that the sorption depends strongly on pH and is more favored at acidic conditions with hydronium ions influence. Hence, the optimal pH value of 4.5 referring to the highest removal efficiency is selected.

Hydrogen chromate ions (HCrO$_4^-$) prevail in an acidic solution leading to the following equilibrium:

$$2HCrO_4^- \Leftrightarrow Cr_2O_7^{2-} + H_2O$$

with pK = 2.05 at standard conditions.

It is evident from the equilibria pointed above that HCrO$_4^-$ ions exist predominantly in an acidic solution with pH ranging from 2.05 to 5.90. The UV-Vis spectra of the solution taken at different operation time show that the initially present peaks at 258 nm and 351 nm shift slightly to 275 nm and 375 nm after 7 min -10 min, respectively (Fig. 7a). The peak shift indicates that dichromate ions are gradually transformed to hydrogen chromate ions. The peak height decreases slightly with further sorption until the latter is over (Fig. 7b). This indicates that chromium (VI) ions removal occurs in absence of any chromium species formation during the sorption.

No change in the visible spectra shape is observed with time longer than 10 min. This means that the sorption could proceeds at the sorbent surface. In other words, the adsorbed chromium (VI) species are reduced forming chromium (III) one. The mechanism of Cr (VI)
removal is generally believed to occur at the sorbent surface following the steps:

1. Cr (VI) sorption on B-ZVI surface where electron transfer takes place;
2. Cr (VI) reduction to Cr(III) under acidic conditions (Eq.2a);
3. Iron oxidation to Fe (III) on the surface (Eq.2b);
4. Precipitation of chromium (III) and iron (III) ions in correspondence with:

\[
\text{Cr}^{3+} + \text{Fe}^{3+} + 4\text{H}_2\text{O} \rightarrow \text{Cr}_n\text{Fe}_{1-x}(OH)_x \downarrow + 3\text{H}^+ \quad (3)
\]

The oxidation/reduction potential (ORP) is a measure of the tendency of gaining or losing electrons due to new species formation in aqueous solutions. The values of ORP and pH of the bulk system are measured as a function of time aiming verification of the mechanism (Fig. 8).

During the operating time the solution pH increases from 4.5 to 8.98, while ORP decreases from 326.1 mV to -6.5 mV because hydrogen chromate ion of a higher ORP is removed from the aqueous medium through adsorption on the surface. The ORP decrease within the first 20 min indicates reduction of chromium (VI) ions to chromium (III) one in the solution. Then it remains almost constant. The residual solution of a lower ORP has the tendency to lose electrons due to the formation of iron (III) and hydroxyl ions in the course of sorption. This means that iron is oxidized both on the surface and in the solution.

The slight change of ORP in the range from 20 min to 60 min is related to iron oxidation to Fe$^{3+}$ and dissolved oxygen reduction to OH$^{-}$ in correspondence with Eq. 4:

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^{-}, \quad E^\circ = 0.40 \text{ V} \quad (4)
\]

This may cause residual solution pH increase to 8 - 9 after 20 min of sorption (Fig. 8).

After that the binding sites of B-ZVI are almost completely occupied because of chromium precipitation (Eq. 3). Consequently, the values of ORP and pH of the residual solution are practically stabilized.

In order to determine the removal efficiency in respect to chromium (VI) ions, chemical analysis of the residual solution is carried out by inductively coupled plasma optical emission spectrometry (Thermo Scientific iCAP7400, USA). The concentrations of chromium and iron ions in the residual solution are found equal to 0.074 mg L$^{-1}$ and 0.555 mg L$^{-1}$, correspondingly. The maximum removal efficiency is estimated equal to 99.85%. The residual amount of iron ions in the solution verifies the proceeding of ZVI oxidation in the batch system (Eq.2b).

**Sorption isotherms**

The experimental data referring to the equilibrium amount of chromium (VI) ions (q$_e$) adsorbed on the B-ZVI and their equilibrium concentration in the bulk of the solution (C$_e$) at the optimal conditions provided are used to find the appropriate isotherm model. The Freundlich and Langmuir isotherms are used in this investigation. Their applicability is evaluated by the linearity expected.

**Freundlich isotherm**

The Freundlich isotherm model assumes that the sorption process takes place on a heterogeneous surface. It is usually presented in the form [49]:

\[
q_e = K_F \cdot C_e^{1/n}
\]

where q$_e$, mg g$^{-1}$ is the amount of chromium (VI) ions adsorbed at equilibrium, C$_e$, mg L$^{-1}$ is the equilibrium chromium (VI) ion concentration in the bulk of the solution, K$_F$, mg$^{1/n}$ g$^{-1}$ L$^n$ is the Freundlich constant related to the bond energy and the sorption capacity, while n is an empirical constant.
The value of $n$ indicates whether the sorption is favorable [50]. Eq. (5) can be linearized, i.e.:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

(6)

A linear plot of $\ln q_e$ versus $\ln C_e$ is plotted. It is presented in Fig. 9, while the calculated parameters are summarized in Table 1.

It is evident that the Freundlich isotherm does not fit well (the correlation coefficient $R^2 > 0.930$) at a relatively low temperature (300 K and 310 K). However it fits well at 320 K.

**Langmuir isotherm**

As one of the first theoretical treatments of nonlinear sorption the Langmuir isotherm has been successfully applied to a wide range of data that exhibit limiting or maximum sorption capacities [49]. The Langmuir isotherm model assumes that (i) a monolayer of sorbate is formed over a uniform sorbent surface; (ii) once a sorbate occupies a site no further sorption can take place at that site; (iii) a saturation value is reached [51]. The distribution of the two phases in contact is controlled by an equilibrium constant. The Langmuir isotherm is expressed as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

(7)

where $q_m$, mg g$^{-1}$ is the sorbate amount adsorbed at equilibrium, $C_e$, mg L$^{-1}$ is equilibrium sorbate concentration in solution, while $q_m$, mg g$^{-1}$ and $K_L$, L mg$^{-1}$ are the maximum sorption capacity and Langmuir constant, respectively. The linear form of Eq. (7) is as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

(8)

Eq. (8) shows that the maximum sorption capacity and the Langmuir constant can be calculated from the slope $(1/q_m)$ and the intercept $1/(q_m K_L)$ of the linear plot $C_e/q_e$ vs. $C_e$ (Fig. 10).

The calculated parameters are listed in Table 1. The constants are evaluated by regression analysis of the experimental data. This is illustrated in Fig. 10. Figs. 9 and 10 show that the Langmuir isotherm describes well chromium (VI) ion sorption on B-ZVI in the temperature range studied. The maximum sorption capacity increases from 54.05 mg g$^{-1}$ to 85.47 mg g$^{-1}$ on temperature increase from 300 K to 320 K, while the Langmuir constant decreases from 0.833 L mg$^{-1}$ to 0.018 L mg$^{-1}$, correspondingly. The equilibrium shifts to desorption with temperature increase and hence $K_L$ decreases. It can be concluded that the sorption occurs favorably at relatively low temperatures.

The Langmuir parameters $q_m$ and $K_L$ are used to evaluate the separation factor ($R_L$) whose value is a measure of the sorption behavior. Thus the sorption is unfavorable if $R_L > 1$, while it is irreversible in case $R_L = 0$. The sorption process is favorable in case $0 < R_L < 1$ [51].

$$R_L = \frac{1}{1 + K_L C_0}$$

(9)

The calculated value of $R_L$ is in the range of 0.013-0.410 indicating that the sorption of chromium (VI) ions on B-ZVI is favorable. It is worth noting that the value of $R_L$ increases with temperature increase. The data obtained in this study provide to conclude that a uni-
form monolayer of $Cr_2Fe(OH)_3$ is formed through chemisorption on the sorbent surface.

### Sorption kinetics

The kinetics of the sorption process is studied. Pseudo I and pseudo II order kinetics models are used.

#### Pseudo first order model

The pseudo first order model can be expressed through the solid surface capacity in the form [52]:

$$\frac{dq}{dt} = k_1 (q_e - q_t)$$  \hspace{1cm} (10)

where $q_e$, mg g$^{-1}$ is the amount of chromium (VI) ions adsorbed at equilibrium, $q_t$, mg g$^{-1}$ is the amount of chromium (VI) ions adsorbed at any time, while $k_1$, min$^{-1}$ is the I order sorption rate constant.

Eq.10 is linearized by integration within the limits of $t$ from 0 to $t$ and $q$ from 0 to $q_t$:

$$\ln(q_e - q_t) = \ln q_e - k_1t$$  \hspace{1cm} (11)

Eq. (11) shows that the pseudo I order sorption rate constant can be calculated from the slope for the linear plot $\ln(q_e - q_t)$ vs. $t$ (Fig. 11). The calculated parameters are listed in Table 2. The correlation coefficient of the graph is poor. This indicates that the kinetics of chromium (VI) ions sorption on B-ZVI does not obey the pseudo I order model in contradiction with the findings of Li na Shi et al. [31, 32]. The value of the correlation coefficient found by them refers to 0.9439 - 0.9863. In fact this was the only model used by these researchers.

#### Pseudo second order model

The pseudo II order rate expression based on the sorption equilibrium capacity can be presented in the form [53].

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2$$  \hspace{1cm} (12)

where $q_e$, mg g$^{-1}$ is the amount of chromium (VI) ions adsorbed at equilibrium, $q_t$, mg g$^{-1}$ is the current amount of adsorbed chromium (VI) ions, while $k_2$, g mg$^{-1}$ min$^{-1}$ is the pseudo II order sorption rate constant.

![Fig. 11. Pseudo first order sorption kinetics of chromium (VI) ions onto B-ZVI at various temperature (pH = 4.5, $C_0$ = 80 mg L$^{-1}$, $T$ = 300-320 K).](image-url)
Eq. (12) is linearized by integration within the limits of \( t \) from 0 to \( t \) and for \( q \) from 0 to \( q \):

\[
\frac{t}{q_t} = q_e^{-1}k_2 + \frac{1}{q_e} \tag{13}
\]

Eq. (13) shows that the pseudo second order rate constant can be calculated from the slope of the linear plot \( t/q_t \) vs. \( t \) (Fig. 12).

The calculated parameters are summarized in Table 2. The data obtained show that a good correlation coefficient is obtained, which in turn indicates that the sorption kinetics of chromium (VI) ions on B-ZVI follows pseudo II order model. The equilibrium sorption capacity obtained is comparable with the experimental values. This implies that the chromium species chemisorption is the rate limiting step [53]. The desorption rate increases with the temperature increase (See Table 1) and hence the equilibrium sorption capacity decreases. The pseudo II order model is successfully applied [36] in describing the sorption of chromium (VI) on montmorillonite (major constituent of bentonite) supported ZVI. Besides Yimin Li et al. [35] suggest that the sorption kinetics of chromium (VI) ions removal using ZVI supported on pillared bentonite follows the Langmuir-Hinshelwood mechanism. They assume that surface catalyzed sorption occurs between chromium (VI) ions and zero valent iron.

Unlike them we advance the following mechanism of the sorption obeying the pseudo II order kinetic model. The heterogeneous reaction with the participation of B-ZVI involves the following steps:

\[
A + S \xrightarrow{k_1} AS \quad k_1, \ min^{-1} \tag{14}
\]

\[
AS + A \rightarrow P \quad k_2 \tag{15}
\]

where \( A \) stands for the binding sites of the sorbent, \( S \) stands for chromium (VI) ion, \( AS \) is the intermediate, while \( P \) is the product.

The sorption of chromium (VI) ions on B-ZVI surface is expressed by Eq. (14). After that mixed hydroxide containing chromium (III) and iron (III) ions is formed on the surface by chromium (VI) ions reduction with zero valent iron (Eq. 15).

The rate law for \( P \) is described by:

\[
\frac{d[P]}{dt} = k_2 [AS][A] \tag{16}
\]

We can use the steady state approximation for \( AS \), i.e.

\[
\frac{d[AS]}{dt} = k_1 [A][S] - k_{-1}[AS] - k_2 [AS][A] \approx 0
\]

The steady state concentration of \( AS \)

\[
[AS] = \frac{k_1 [A][S]}{k_{-1} + k_2 [A]}
\]

can be found and then substituted in Eq. (16) to give:

\[
\frac{d[P]}{dt} = \frac{k_1 k_2 [A]^2 [S]}{k_{-1} + k_2 [A]} = k_{2nd} [A]^2 [S] \tag{17}
\]

Table 2. Calculated rate constants for pseudo first and second order models.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Pseudo first order</th>
<th>Pseudo second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k_1, \ min^{-1} )</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>300</td>
<td>0.0296</td>
<td>0.8164</td>
</tr>
<tr>
<td>310</td>
<td>0.0971</td>
<td>0.8621</td>
</tr>
<tr>
<td>320</td>
<td>0.1523</td>
<td>0.7186</td>
</tr>
</tbody>
</table>
where $k_{2m}$ is the effective rate constant.

The first step ($k_1$) is the rate determining one because $k_1$ has to be much smaller than $k_2$ and $k_2$, while the intermediate concentration can be assumed almost constant [54].

The overall sorption kinetic rate law can be expressed through Eq. (12) taking into consideration that the amount of sorption is proportional to the number of binding sites occupied on ZVI surface and the concentration of chromium (VI) ions is constant. This is in accord with the evidence that the sorption kinetics of chromium (VI) species on B-ZVI obeys the pseudo II kinetic order model.

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The activation energy value is evaluated from the slope of the linear plot (Fig. 13).

The activation energy value is found equal to 107.47 kJ mol$^{-1}$. Hence, it is evident that the sorption of chromium (VI) ions on B-ZVI most likely involves chemisorption of the mixed hydroxide on B-ZVI surface.

**Thermodynamics for sorption of chromium (VI) ions onto B-ZVI**

The standard Gibbs energy of sorption, $\Delta G^\circ$ can be expressed through the equilibrium constant ($K$):

$$\ln K = -\frac{E_a}{RT} + \text{const}$$

where $R$ is the universal gas constant (equal to 8.314 J mol$^{-1}$ K$^{-1}$), $T$ is the temperature, while $K_L$ is the Langmuir equilibrium constant.

This thermodynamic relation is used to calculate the equilibrium constant of sorption from the thermodynamic data and to predict the equilibrium composition of the reaction mixture. The values of the standard entropy change, $\Delta S^\circ$ and enthalpy change, $\Delta H^\circ$ of sorption can be used to obtain the standard Gibbs energy of sorption, $\Delta G^\circ$:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

By combining Eqs. (20) and (21)

$$\Delta G^\circ = -RT \ln K_L$$

Eq. (22) shows that the standard entropy, $\Delta S^\circ$, and enthalpy, $\Delta H^\circ$, of sorption can be calculated from the slope ($-\Delta H^\circ/R$) and the intercept ($\Delta S^\circ/R$) of the linear plot $\ln K$ versus $1/T$ (Fig.14).

The calculated parameters are presented in Table 3.

![Fig. 13. Linear plot of lnk versus 1/T.](image)

![Fig. 14. The linear plot lnK versus 1/T of sorption.](image)
The values obtained can evidence that chromium (VI) ions chemisorb on B-ZVI. The negative sign of the standard enthalpy change, $\Delta H^\circ$, indicates that the sorption considered is exothermic. The typical sorption enthalpy values are about 20 kJ mol$^{-1}$ for physisorption and 200 kJ mol$^{-1}$ for chemisorption [54]. Table 3 shows that the value of the enthalpy change amounts to -151.2 kJ mol$^{-1}$, i.e. chemisorption seems more feasible. The negative sign of the entropy change indicates that chromium (VI) species are formed on B-ZVI surface through chemisorption building a stable structure on the solid surface. A spontaneous process requires $\Delta G^\circ < 0$. Since $\Delta S^\circ$ and $\Delta H^\circ$ are negative, the sorption has to be favored by temperature decrease. When the temperature is raised, $\Delta G^\circ$ increases and equilibrium constant decreases. This results in equilibrium shift to left.

CONCLUSIONS

Our study shows that supporting ZVI with bentonite overcomes ZVI disadvantages. The bentonite supported zero valent iron is an effective sorbent for removal of chromium (VI) species from aqueous media. The maximum removal amounts to 99.85 % at optimal conditions referring to initial pH of 4.5, a sorbent dosage of 0.3 g and an initial chromium concentration of 50 mg L$^{-1}$.

The Langmuir isotherm is the best model describing chromium (VI) ion sorption on B-ZVI in the temperature range selected. The kinetics of chromium (VI) ions sorption on B-ZVI follows the pseudo II order model. A uniform monolayer of a mixed hydroxide is formed on the surface through chemisorption. The thermodynamic data show that the sorption occurs spontaneously and is favored by temperature decrease. It is viable to determine the optimal temperature and control the sorption process on account of the kinetic and thermodynamic stability at lower temperatures.

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