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# Removal of zinc from a metal plating wastewater using an Iranian sepiolite: determination of optimum conditions

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ABSTRACT

Removal of heavy metals from industrial wastewaters has recently received a lot of attention. Limited information is available about the feasibility of using clay minerals to remove heavy metals from the real wastewaters. This study was conducted to assess the influence of several variables including contact time, suspension pH (5, 7, and 9), temperature (20 and 40˚C), size (< 2 μm, 2–20 μm, and 20–50 μm), and amount (2, 4, 8, 12, 16, and 20 g $l^{-1}$) of sepiolite application on the adsorption and removal of $Zn^{2+}$ ions from a real metal plating wastewater. Results showed that the sorption of Zn on Iranian sepiolite is a relatively fast process with the equilibrium being attained within 12 h after the sorbent application. Results also illustrated that the removal efficiency of $Zn^{2+}$ ions increases with the increase in suspension pH from 5 to 9, and dose of sepiolite application from 2 to 16 g $l^{-1}$. However, a decrease in sorbent size from 20–50 μm to < 2 μm favored the removal of $Zn^{2+}$ ions from the wastewater studied. The results also indicated the sorption of Zn onto sepiolite as the temperature increased from 20 to 40˚C. Iranian sepiolite appears to have a high potential to remove more than 95% of the total concentration of $Zn^{2+}$ ions from the metal plating wastewater studied under the optimized conditions.

*Keywords:* Zinc; Wastewater; Sepiolite; Adsorption; Kinetics

## 1. Introduction

With the rapid development of industries such as metal plating facilities, mining, fertilizer producing industries, tanneries, and paper industries, heavy metals enriched wastewaters are directly or indirectly discharged into the environment [1]. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms. Toxic heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead, and chromium [1]. Zinc is a trace element that is essential for human health. It is important for the physiological functions of living tissues and regulates many biochemical processes. However, too much zinc can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea, and anemia [2].

A variety of methods including chemical precipitation, ion exchange, and adsorption have been developed over the years to remove heavy metals from our environment [3]. Adsorption has been proven to be an excellent and cheap method to remove hazardous materials such as heavy metals and

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organic dyes from waste effluents [4]. Although activated carbon is widely used as an adsorbent material, it is relatively expensive. This decreases the application of activated carbon in many industries. That is why many investigators have searched for low-cost and locally available substitutes to remove heavy metals from wastewaters [5]. Clay minerals such as sepiolite and palygorskite are widely distributed in arid and semiarid regions of the world [6]. Sepiolite has a ribbon-like structure and is formed from two inversed silica tetrahedral sheets and a magnesium octahedral sheet between them making alternate hollow channels allowing penetration of solutes into the structure. In addition, some isomorphic substitutions in the tetrahedral layer, such as $Al^{3+}$ for $Si^{4+}$, develop negatively charged adsorption sites. Such sites are able to adsorb cations and compensate their charge [6,7]. Due to the above structural characteristics as well as the chemical and mechanical stability, these minerals have received a great attention for the removal of heavy metals from wastewaters.

Among the most important factors affecting adsorption are particle size and dose of adsorbent, contact time, pH, and the solubility of adsorbate in liquid [1,3]. It has been approved that the application of adsorbents with smaller size, and higher dose of application under equilibrium conditions increases the adsorption efficiency [3,5]. However, the preparation of smaller particles and application of higher doses of adsorbents increases the cost of materials and consequently the cost of removal procedure. Therefore, a higher efficiency of the adsorption techniques could be achieved via a proper design of sorption processes. This needs a thorough understanding of the reaction pathways, the mechanisms of sorption reactions, and the rate of solute uptake at the solid–liquid interface. The study of the kinetics and thermodynamics of the adsorption process could, therefore, provide such information [8]. This study aims to investigate the influence of factors such as contact time, initial pH of suspension, adsorbent dose, and particle size of adsorbents on removal capacity of sepiolite for zinc ions from wastewaters of a metal plating industry.

## 2. Materials and methods

### 2.1. Wastewater sample

The wastewater sample used in this study was taken from a zinc metal plating facility in Tehran, northern Iran. The wastewater sample was analyzed for pH, electrical conductivity (EC), the total concentration of dissolved solids, turbidity, and the total concentration of Zn, Fe, Mg, Pb, and Cd ions. The concentration of Zn and other heavy metals was determined using a Savant GBC Atomic Absorption Spectrophotometer (AAS) with the detection limits of 8, 50, 3, 60, 8, and 9 ppb for Zn, Fe, Mg, Pb, and Cd, respectively.

### 2.2. Materials and reagents

The sepiolite sample used in this study was taken from a mine in Fariman region, northeastern Iran. The chemical composition and physicochemical characteristics of Fariman sepiolite are given in Tables 1 and 2, respectively.

The mineralogical composition of the samples was determined by a Philips PW 1840 X-ray diffractometer, and the semi-quantitative analysis was based on the XRD pattern of non-oriented powder sample using the method described by Schultz [9]. Total elemental analysis of the sepiolite sample was determined using a X-ray Fluorescence Spectrometer, Bruker S4 Pioneer. The specific surface area and cation exchange capacity of the samples were measured by $N_2$-BET sorption analysis and $NH_4$-acetate method, respectively. All chemicals employed in this study were analytical grade and used with no pretreatment.

### 2.3. Zeta potential

The zeta potential of sepiolite suspensions was measured as a function of equilibrium pH ranging from 2–10 using a ZEN 3600 equipped with a microprocessor unit. The unit automatically calculates the electrophoretic mobility of the particles and converts it to the zeta potential. A suspension of 0.1 g sepiolite in

Table 1
Chemical and mineralogical composition of sepiolite sample employed in the study

| Property | Value |
|---|---|
| $SiO_2$ (%) | 55.32 |
| $Al_2O_3$ (%) | 0.30 |
| MgO (%) | 15.73 |
| $Na_2O$ (%) | 0.02 |
| $K_2O$ (%) | 0.01 |
| $TiO_2$ (%) | 0.02 |
| MnO (%) | 0.00 |
| CaO (%) | 2.74 |
| $P_2O_5$ (%) | 0.00 |
| $Fe_2O_3$ (%) | 0.59 |
| $SO_3$ (%) | 0.00 |
| LOI (%) | 25.11 |
| Total (%) | 99.84 |
| Mineralogical composition (%) | Sepiolite (70%), Quartz (15%), Dolomite (15%) |

Table 2
Physicochemical properties of sepiolite samples (<2 μm and 20–50 μm) employed in this study

| Property | <2 μm | 2–20 μm | 20–50 μm |
|---|---|---|---|
| Specific surface area ($m^2g^{-1}$) | 321.3 | 233.1 | 179.9 |
| Specific total volume pore ($cm^3g^{-1}$) | 0.622 | 0.469 | 0.378 |
| Cation exchange capacity (cmol (+) $kg^{-1}$) | 13.1 | 12.2 | 11.8 |

80 mL distilled water was shaken in an orbital shaker incubator and rinsed for 24 h at 20 ± 1℃. The average of five measurements was used to represent the measured potential. The applied voltage during the measurements varied in the range of 50–150 mV [10].

### 2.4. Kinetic experiments

All sorption studies were performed using the batch technique because of its simplicity and reliability [11]. The experiments were conducted at pH = 5, sorbent concentration of 2 $gl^{-1}$, sorbent size of 20–50 μm, and at the temperature of 20 ± 1℃.

To investigate the effect of contact time on the adsorption processes a constant mass of sepiolite (adsorbent) (0.1 g) and 50 ml of known concentration of wastewater were added to 80 ml polypropylene centrifuge tubes. The mixtures were shaken vigorously on an orbital shaker (175 rpm) at specified times (5, 10, 15, 20, 30, 60, 120, 240, 480, 720, 1,440, and 2,880 min). Tubes were then removed from the shaker and centrifuged at 2,500 rpm for 25 min and the Zn concentration in the supernatant was measured using AAS.

In order to investigate the effects of suspension pH and temperature, adsorbent dose, and particle size of adsorbents on the percentage removal of Zn, the above experiments were also run by varying initial pH of suspension (5, 7, and 9 after adjustment using dilute NaOH and HCl solutions), temperature (20 and 40℃ using a thermostatic shaker bath) adsorbent dose (2, 4, 8, 12, 16, and 20 $gl^{-1}$), and particle size of adsorbent (<2, 2–20, and 20–50 μm) while keeping all other parameters constant. All the experiments were carried out using the largest size and lowest amount of sorbents to identify how removal efficiency is affected if smaller size of particles and higher doses of sepiolite are applied.

Control treatments with no addition of adsorbent were also run to test the possible adsorption and/or precipitation of Zn onto the container walls. Preliminary experiments showed that metal losses due to the adsorption onto the container walls were negligible.

The amount of $Zn^{2+}$ adsorbed by sepiolite, $C_S$ (mg $g^{-1}$), was obtained as follow:

$$C_S = \frac{[(C_0 - C_e)] \cdot V}{M} \tag{1}$$

where $C_0$ and $C_e$ ($mgl^{-1}$) are the initial and final (equilibrium) concentrations of Zn, respectively, V (ml) is the volume of solution, and M is the mass of sorbent (mg). All measurements were carried out with three replications.

Satisfactory conformity between experimental data and the model predicted values was evaluated by correlation coefficient ($r^2$) and non-linear Chi-square ($\chi^2$). The $\chi^2$ values were calculated using Eq. (2):

$$\chi^2 = \sum \frac{(C_S - C'_S)^2}{C'_S} \tag{2}$$

where $C_S$ and $C'_S$ are measured and model estimated amount of Zn sorbed at equilibrium, respectively, and $n$ is the number of measurements. If data from the model are similar to experimental data, $\chi^2$ will be low and if they differ, $\chi^2$ will be high [12].

## 3. Results and discussion

### 3.1. Physicochemical characteristics of wastewater

Physicochemical analyses of wastewater sample (Table 3) show that the wastewater is acidic, and contains high concentration of Zn (285.5 mg $L^{-1}$) and dissolved solids. However, the concentration of other heavy metals is significantly less than that of Zn.

### 3.2. Kinetic studies

Contact time is an important parameter because it can reflect the adsorption kinetics of an adsorbent for a given initial concentration of adsorbate [13]. Fig. 1 shows the effect of contact time and temperature on the adsorption capacity of sepiolite for $Zn^{2+}$ ions. The results show that the sorption of $Zn^{2+}$ ions is rapid during the first 240 min of the experiment and thereafter it is followed by a relatively slower rate until the equilibrium reaches at 720 min. The initial rapid phase may be due to the increase in the number of vacant sites and also the high concentration gradient between adsorbate in solution and that in the adsorbent. With the decrease in gradient between adsorbate concentration in solution and that on the adsorbent surface, the

Table 3
Some physicochemical characteristics of the wastewater studied

| Property | Value |
|---|---|
| Colour | Yellow |
| Electrical conductivity (dS/m) | 5.05 |
| Total dissolved solids (mg $l^{-1}$) | 3,230 |
| pH | 6.06 |
| Zn (mg $l^{-1}$) | 285.53 |
| Fe (mg $l^{-1}$) | 5.20 |
| Mg (mg $l^{-1}$) | 3.19 |
| Pb (mg $l^{-1}$) | 7.79 |
| Cd (mg $l^{-1}$) | 1.09 |
| Turbidity (NTU) | 37.5 |

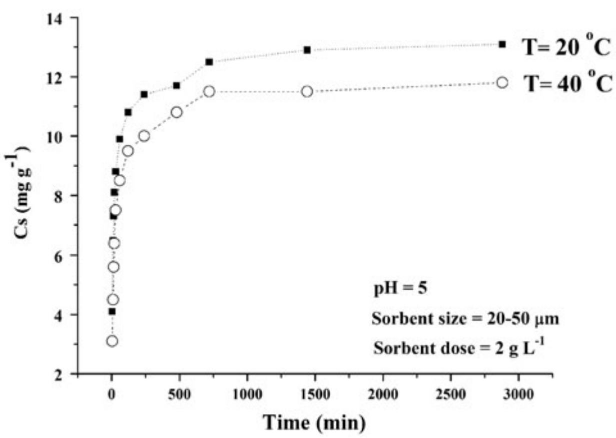


Fig. 1. Effects of contact time and suspension temperature on the adsorption capacity of sepiolite particles for $Zn^{2+}$ ions.

rate of adsorption decreases until the equilibrium conditions is attained and the surface of adsorbent is saturated by adsorbate [14].

According to Fig. 1, as the temperature increases from 20 to 40℃, the adsorption capacity of sepiolite for $Zn^{2+}$ decreases from 13.1 to 11.8 mg $g^{-1}$. The decrease in removal capacity of $Zn^{2+}$ ion with the rise in temperature is probably due to an increase in desorption of $Zn^{2+}$ ion from the minerals interface to the solution. This also confirms that at high temperature, adsorption of $Zn^{2+}$ onto sepiolite could be considered as an exothermic phenomenon [15,16].

In order to identify the adsorption kinetics of $Zn^{2+}$ ions on sepiolite and the effects of temperature on the adsorption kinetics of $Zn^{2+}$, two kinetic models including pseudo-first-order and pseudo-second-order were employed (Table 4; Figs. 2 and 3). The linear form of pseudo-first-order kinetic model is as below:

$$\mathrm{Log}(C_S - C_T) = \mathrm{Log}C_S - \frac{K_1 \cdot T}{2.303} \tag{3}$$

where $C_T$ (mg $g^{-1}$) is the adsorption capacity at time $T$ and $K_1$ ($min^{-1}$) is the rate constant of the pseudo-first-order model [17]. The value of $K_1$ was determined from the slope of the plot Log ($C_s$-$C_T$) vs. $T$.

The kinetic data were also analyzed using pseudo-second-order kinetic model of Ho and Mc Kay [18], expressed as Eq. 4:

$$\frac{T}{C_T} = \frac{1}{K_2 \cdot C_S^2} + \frac{1}{C_S}, \tag{4}$$

where $K_2$ (g $mg^{-1}$ $min^{-1}$) is the rate constant of pseudo-second-order adsorption and $K_2 \cdot C_S^2$ or h (mg $g^{-1}$ $min^{-1}$) is the initial rate of adsorption reaction. These parameters were determined experimentally from the slope and intercept of plot $T/C_T$ vs. T.

As compared to the pseudo-first-order kinetic model, a very good correlation coefficient ($r^2$) was obtained for the pseudo-second-order kinetic model (Fig. 3; Table 4). Besides, when $\chi^2$ values of pseudo-first-order kinetic model (19.187) and that of the pseudo-second-order kinetic model (0.001) are compared, it can be concluded that the adsorption of $Zn^{2+}$ ions onto the sepiolite particles follows the pseudo-second-order kinetic model.

Table 4
Rate constants of $Zn^{2+}$ adsorption on sepiolite particles as estimated from the pseudo first- and second-order kinetic models at different temperatures

| | | Pseudo first-order | | | Pseudo second-order | | | |
|---|---|---|---|---|---|---|---|---|
| Temperature (℃) | $C_S$ (mg $g^{-1}$) | $K_1$ ($min^{-1}$) | $C'_S$ (mg $g^{-1}$) | $R^2$ | $K_2$ (g $mg^{-1}$ $min^{-1}$) | $C'_S$ (mg $g^{-1}$) | h (mg $g^{-1}$ $min^{-1}$) | $R^2$ |
| 20 | 13.1 | 0.0023 | 5.36 | 0.857 | 0.0024 | 13.15 | 0.41 | 0.999 |
| 40 | 11.8 | 0.0023 | 5.29 | 0.831 | 0.0016 | 11.90 | 0.23 | 0.999 |

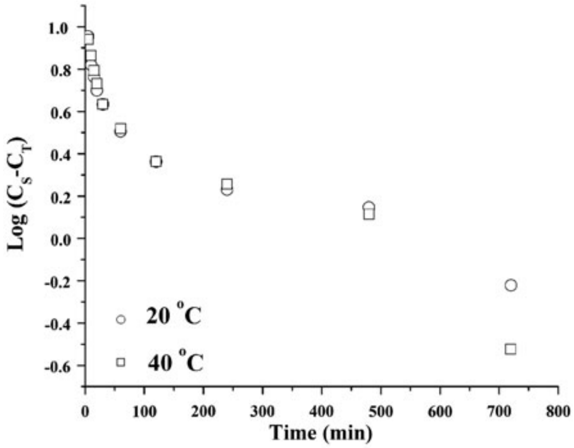


Fig. 2. Pseudo first-order plot for the removal of $Zn^{2+}$ ions from the wastewater using sepiolite at different temperatures.

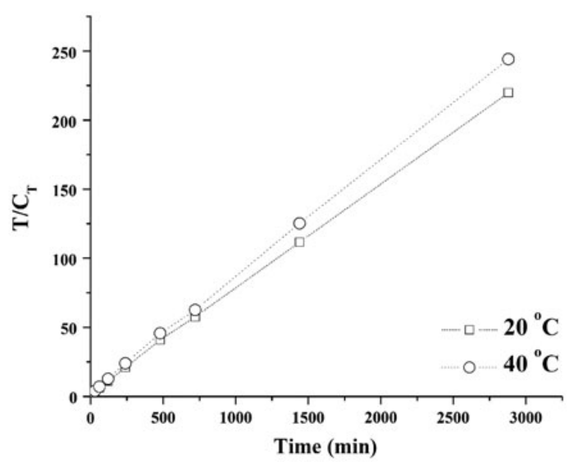


Fig. 3. Pseudo second-order plot for removal of $Zn^{2+}$ ions from the wastewater using sepiolite at different temperatures.

Results also imply that with the increase in temperature from 20 to 40°C, the rate constant ($K_2$) and the initial adsorption rate (h) of pseudo-second-order model (as the best model) shows a decreasing pattern. This further confirms the exothermic nature of the process of removal (Table 4). Similar results were also reported by Sharma [19] for the removal of $Cd^{2+}$ ions from a synthetic solution using an indigenous clay from China.

### 3.3. Effects of pH

The influence of pH on removal efficiency of $Zn^{2+}$ by sepiolite (Fig. 4) shows that the adsorption of $Zn^{2+}$ ions increases with an increase in pH of the solution. It is known that clays possess a negative surface charge in solution [15]. As pH changes, surface charge also changes, and the adsorption of charged species is affected. In this study, the point of zero charge of sepiolite particles was determined at pH = 6.4 ± 0.2 [Fig. 5]. The increase in zinc ($Zn^{2+}$) adsorption with increasing pH is similar to the adsorption pattern of other hydrolysable metal cations. It is known from the literature that Zn species are present in deionized water in the forms of $Zn^{2+}$, $Zn(OH)^+$, $Zn(OH)_{2(S)}$, etc [20]. At pH~5.0, the solubility of the $Zn(OH)_{2(S)}$ is high and; therefore, the $Zn^{2+}$ is the main species in the solution [21]. Therefore, at pH = 5 (lower than the point of zero charge), where there is an excess of $H_3O^+$ ions in solution, the exchange sites on the sepiolite particles become more positive and the $Zn^{2+}$ ions compete with the $H^+$ ions in the solution for the active sites and the adsorption of $Zn^{2+}$ ions onto sepiolite particles consequently decreases [22,23]. As the pH increases, the solubility of $Zn(OH)_{2(S)}$ decreases and at pH values above that of the point of zero charge, sepiolite surface has a higher negative charge which results in higher adsorption of $Zn^{2+}$ ions [24,25]. At pH~10.0, the solubility of $Zn(OH)_{2(s)}$ is very small [21]. Under such pH conditions, the main species in the solution is $Zn(OH)_{2(S)}$. Therefore, in the alkaline range, the metal ion precipitation plays the main role in the removal of the $Zn^{2+}$ ions attributed to the formation of precipitate of $Zn(OH)_{2(S)}$ [26]. Similar results were also reported by other researchers [20,21,27].

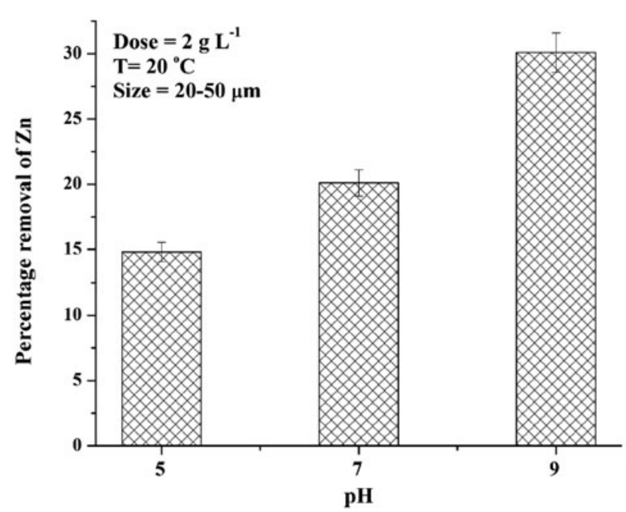


Fig. 4. Effect of the initial pH of suspension on the percentage removal of $Zn^{2+}$ ions from the wastewater.

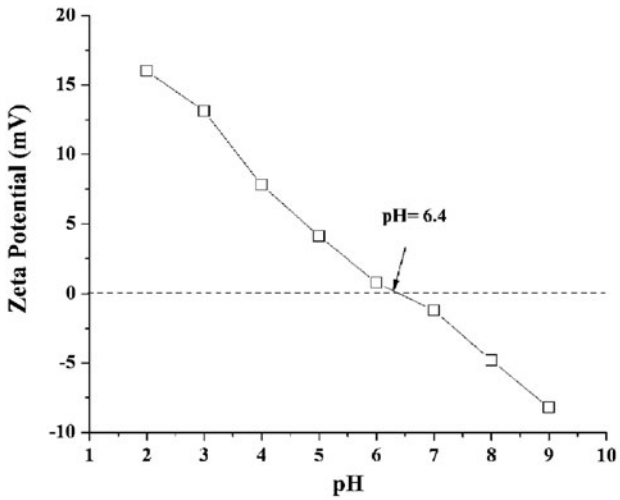


Fig. 5. Zeta potential of sepiolite particles as a function of equilibrium pH.

### 3.4. Effects of adsorbent size

The results of the effect of sepiolite particle size on the removal efficiency of $Zn^{2+}$ ions from wastewater (Fig. 6) indicates that as the particle size decreases, the metal diffusion is induced. This increases the accessibility of $Zn^{2+}$ ions by the mineral [28]. This suggests that the most suitable particle size of sepiolite for the removal of $Zn^{2+}$ ions from wastewater studied is < 2 μm.

### 3.5. Effects of adsorbent dose

The amount of adsorbent is an important factor determining the sorption capacity of an adsorbent for a given initial concentration of sorbate [3, 29]. The influence of sepiolite dosage on the removal efficiency of $Zn^{2+}$ ions is given in Fig. 7. As expected, the percent removal of $Zn^{2+}$ ions increases as the amount of sepiolite increases [30, 31]. This can be attributed to an increase in the number of sorbent sites after the addition of more mineral particles to the suspension. Similar results were also reported by Kaya and Ören [20]. Based on this, the application dose of 16 g $l^{-1}$ could be suggested as the optimum amount of sepiolite application for treatments of the wastewater studied.

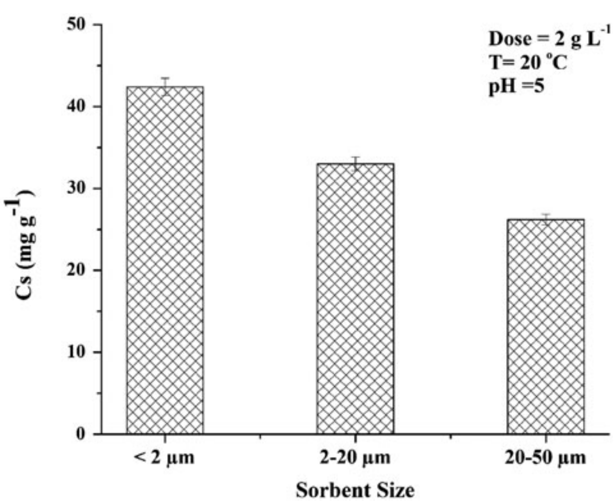


Fig. 6. Effect of the size of sepiolite particles on adsorption of $Zn^{2+}$ ions.

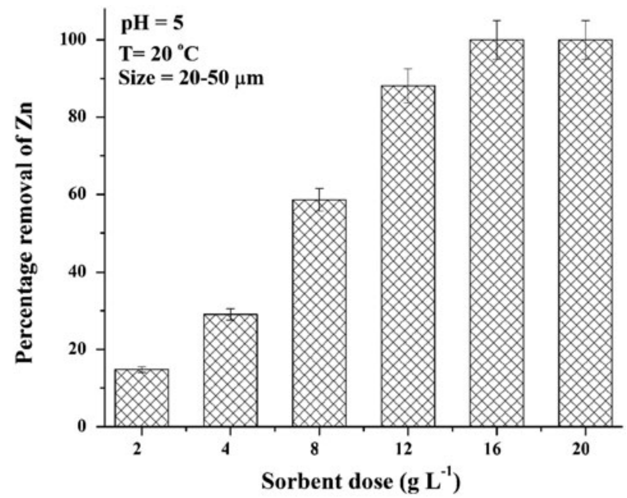


Fig. 7. Effect of sepiolite dose of application on percentage removal of $Zn^{2+}$ ions from the studied wastewater.

### 3.6. Effects of optimized conditions on characteristics of wastewater

Characteristics of the wastewater after treatment with the sepiolite particles under the optimized conditions (suspension pH = 9, contact time = 720 min,

Table 5
Characterization of wastewater after treatment with sepiolite under the optimized conditions

| Property | Value |
|---|---|
| Electrical conductivity (dS/m) | 2.31 |
| Total dissolved solids (mg $l^{-1}$) | 1,480 |
| Zn (mg $l^{-1}$) | 13.71 |
| Fe (mg $l^{-1}$) | 2.80 |
| Mg (mg $l^{-1}$) | 3.31 |
| Pb (mg $l^{-1}$) | 2.51 |
| Cd (mg $l^{-1}$) | 0.83 |
| Turbidity (NTU) | 14.9 |

dose = 16 g $L^{-1}$, and size = < 2 μm) are shown in Table 5. Results clearly indicate that the application of sepiolite particles could remove more than 95% of the total concentration of $Zn^{2+}$ ions from the wastewater and reduced the EC and the total content of dissolved solids. This confirms the suitability of Iranian sepiolite as a good adsorbent for removal of $Zn^{2+}$ ions from studied wastewater.

## 4. Conclusions

Iranian sepiolite was proven to be an effective adsorbent for the removal of $Zn^{2+}$ ions from metal plating wastewaters. This study clearly shows that the adsorption of $Zn^{2+}$ ions from the studied wastewater is strongly dependent on the initial pH and temperature of solutions. It was also observed that an increase in temperature results in a lower metal loading per weight unit of sepiolite particles. However, increasing the initial pH of suspension increased the efficiency of removal. It is concluded that the basic mechanism that governs the removal of zinc at pH ranging from 5 to 9 are adsorption onto sepiolite particles and the chemical precipitation from solution. Kinetic studies show that the adsorption is a three-stage process including a fast initial phase, a second slow phase, and then an equilibrium condition. Based on the kinetic studies, the pseudo-second-order kinetic model fits very well with the adsorption behavior of $Zn^{2+}$ ions onto the Iranian sepiolite. The optimum conditions for the removal of $Zn^{2+}$ ions from the studied wastewater were determined as pH 9, suspension temperature of 20˚C, sepiolite particle size of < 2 μm, and the sorbent application dose of 16 g $l^{-1}$. Under these optimum conditions, application of sepiolite particles could remove more than 95% of the total concentration of $Zn^{2+}$ ions from the metal plating wastewater studied.

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