

Comparison of the effectiveness of natural dolomite and modified dolomite in the removal of heavy metals from aqueous solutions

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Date of submission: 14 Sep 2018, **Date of acceptance:** 23 Jan 2019

ABSTRACT

Presence of heavy metals in water resources is a critical environmental challenge in various communities. To date, various methods have been applied to remove heavy metals, such as the use of cost-efficient materials. The present study aimed to evaluate the adsorption of heavy metals (iron, zinc, nickel, lead, and cadmium) on dolomite and thermally-modified dolomite. We assessed the potentials of natural and thermally-modified dolomite in terms of the adsorption of heavy metals from aqueous solutions. The samples were analyzed to determine the concentrations of metal ions using Spectra 200 Varian. For the optimization and evaluation of the influential factors in the adsorption amount, factors such as the initial concentration of the solution, pH, contact time, and adsorbent dosage were considered. Comparison of the final removal results indicated that lead and cadmium had the shortest contact time (15 minutes), while the longest contact time belonged to iron and nickel (60 minutes). In addition, the highest and lowest removal efficiency within the optimum time was 99% and 93% for cadmium and iron, respectively, while the minimum dosage of the optimum adsorbent belonged to iron and zinc. The minimum removal efficiency belonged to nickel (3 mg/l), while the maximum removal efficiency was obtained for cadmium, iron, and zinc (10, 5, and 5 mg/l) with the concentrations of 99%. According to the results, modified dolomite has great potential to remove metals and heavy metals.

Keywords: Dolomite, Natural Dolomite, Modified Dolomite, Heavy Metals

Introduction

Today, protecting the environment against the pollutions caused by modern industries and technologies is a grave concern. Heavy metals have high toxicity even at extremely low concentrations and are particularly harmful to the environment and health.¹ Unlike organic pollutants, metals are not decomposed through chemical reactions or biological processes, but rather, their composition changes, and they remain in the environment until their concentrations increase in the food chain and in living organisms.²

Iron is an abundant element on this planet, constituting approximately 5% of the Earth's crust. Iron is mostly found in natural

water resources. The overconcentration of iron in the human body leads to hemochromatosis and increases the intestinal absorption of this element, along with sediments in various other tissues, such as the liver, heart, pancreas, joints, and pituitary tissues.

Nickel is a heavy metal that is frequently found in industrial effluents.³ High concentrations of nickel have been observed in silver purification, steel production, casting, and textile printing effluents. Zinc is another toxic heavy metal, which has a bluish white color. This element accounts for the bitter and unpleasant taste of water.

Lead is another highly toxic heavy metal, which enters water, soil, and air through aeration and the chemical erosion of minerals, thereby entering the food chain through penetrating herbal tissues. Cadmium is another substantially important heavy metal, which causes toxicity in humans even at low concentrations and leads to renal damage,

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Citation: Imen Z, Hassani AH, Borghae SM. Comparison of the effectiveness of natural dolomite and modified dolomite in the removal of heavy metals from aqueous solutions. J Adv Environ Health Res 2019; 7(1): 61-74

carcinogenic effects, and other damages. In the current research, the term dolomite has been used to refer to a substance composed of calcium magnesium carbonate.^{4,6} The chemical formula of calcium magnesium carbonate is $\text{CaMg}(\text{CO}_3)$; this mineral is found in cream and grayish-white colors, while its other types are also found in white, yellow, green, and black colors. Calcium magnesium carbonate has a density of 2.6 g/cm^3 , hardness of 3.5-4, and vitreous luster.

Dolomite is mainly composed of magnesium oxide (MgO) and lime (CaO).^{7,8} In recent years, this substance has attracted the attention of researchers as a cost-efficient alternative to the costly adsorbents that are capable of removing heavy metals from polluted water. As a result, dolomite could replace the costly methods of heavy metal removal from aqueous solutions. The removal of heavy metals using these minerals is a mechanism involving ion exchange and carbon sequestration.^{9,10}

Calcined dolomite is composed of calcium oxide (CaO) and magnesium oxide (MgO) and is obtained by heating the dolomite ore in a furnace. In fact, thermal processing or calcination is based on the fact that magnesium carbonate is decomposed at the temperature of $800 \text{ }^\circ\text{C}$, leading to chemical changes in the porosity and surface area of minerals.^{11,12}

MgO and CaO are formed completely separately and are not mutually soluble. These processes are classified as thermal procedures, during which carbonate is calcined to lose CO_2 . Calcination is defined as the heating of a mineral at relatively high temperatures in the presence of air and below the melting point of the mineral for the removal of moisture, carbonic acid, sulfur, and other volatile substances. Calcination increases the ore with the same size and higher porosity. The carbonate calcination reaction is a heterogeneous, endothermic reaction, in which a carbonate transforms into the solid phase (calcined carbonate) and gas phase (CO_2) through receiving external heat. Some thermal degradation methods (e.g., thermogravimetry, differential thermal analysis, and differential scanning calorimetry) are used to determine the calcination temperature of

these carbonates. Moreover, extensive research has been focused on the thermal degradation of dolomite in the presence of air and in the base form. Dolomite decomposition occurs in two independent stages with the adequate partial pressure of CO_2 .^{11,13}

In the current research, dolomite was purchased from the Iranian Refractories Procurement Production Company. In 1991, a study was conducted to examine the possibility of phosphorus removal from wastewater through fixation with half-burned dolomite grains. The obtained results demonstrated the formation of non-stoichiometric calcium phosphate on the surface of the grains. From an engineering perspective, this treatment could serve as a tertiary step after the biological treatment of wastewater. In addition, finely pulverized powder (diameter $<100 \mu\text{m}$) should be directly added to the outlet of a poor axial mix aeration basin in order for the powder to incorporate into the biological floc, which in turn enhances the separation of the sludge in the sedimentation tank.¹⁴

In this regard, Walker *et al.* reported that charred dolomite could potentially act as an adsorbent in the removal of brilliant red reactive dye (Levafix brilliant red E-4BA) from aqueous solutions. Furthermore, the effects of initial dye concentration, adsorbent mass, liquid volume ratio, and agitation speed on dye removal have been determined based on the experimental data and mathematically described using burnt dolomite, representing an effective adsorbent with the removal rate heavily depending on external mass transfer and intra-particle diffusion.¹⁴

Takht Kose *et al.* used the dolomite resulting from stone industries as a cost-effective adsorbent for the removal of lead from aqueous solutions. In order to examine the effects of various factors on the adsorption surface, the mixing speed and adsorbent dosage were evaluated *in-vitro*. The experimental results indicated that the dolomite resulting from stone wastes could be used as an inexpensive, highly-effective adsorbent for the removal of $\text{Pb}(\text{II})$ with an efficiency of more than 99%.⁷

Jamalinejad *et al.* mainly attempted to investigate the performance of the dolomite wastes resulting from stone industries as an adsorbent for the removal of dyes from textile effluents. The findings indicated the high efficiency of the selected adsorbent in the removal of dyes. Freundlich adsorption isotherm is considered to be the optimal descriptor of dye adsorption using burnt dolomite in the state of equilibrium.¹⁵

In another research to removal of lead from an aqueous medium using rice husk, sawdust, and sunflower stem reported that the absorption efficiency of each absorbent increased as the input lead concentration reduced from 80 to one mg/l, so that the absorption efficiency of different absorbents was observed to converge. Furthermore, absorption efficiency was reported to increase with mass.¹⁶

Pehlivan *et al.* used natural Turkish dolomite to remove Cu and Pb from aqueous solutions, and more than 85% of the studied cations was removed by dolomite from the aqueous solutions in that phase. Moreover, the mentioned study aimed to assess the efficiency of raw dolomite as an available, inexpensive material, which is found abundantly across the world, as well as in Iran.¹⁷

The present study aimed to compare the effectiveness of natural and thermally-modified dolomite in the removal of heavy metals (iron, zinc, nickel, lead, and cadmium) from aqueous solutions, investigate the adsorption potential of Iranian dolomite as a cost-efficient adsorbent in the removal of iron, zinc, nickel, lead, and cadmium ions from aqueous solutions, and compare the effectiveness of natural dolomite and modified dolomite in the removal of their ions. To this end, we modified dolomite by heating for its comparison with natural dolomite in the removal of heavy metals from aqueous solutions to achieve efficiency in the outcomes.

Materials and Methods

In this experimental study, natural and modified dolomite (obtained from the hot springs in North Khorasan province, Iran) were provided by the Iranian Refractories Procurement and Production Company and used

as adsorbents for the removal of heavy metals. The experiments were conducted in four steps *in-vitro* in a batch reactor under optimum conditions in terms of the contact time, adsorbent dosage, initial heavy metal concentration, and pH.

Initially, 100 mg/l of the stock solutions of the heavy metals was prepared using the metal salts and mixed with distilled water (Gesellschaft für Labortechnik mbH [GFL]) in order to increase the volume of the solution to one liter. To prepare the zinc stock solution with the atomic mass of 65 g/mol, 0.401 g of $Zn(NO_3)_2 \cdot 4H_2O$ metal salt (Merck, Germany) was used. In addition, the iron stock solution with the atomic mass of 56 g/mol was prepared using 0.275 g of $Fe(NO_3)_2 \cdot 9H_2O$ metal salt (Merck, Germany). The cadmium stock solution with the atomic mass of 112 g/mol was prepared using 0.275 g of the metal salt, the nickel stock solution was prepared with the atomic mass of 59 g/mol using 0.439 g of the metal salt, and the lead stock solution was prepared with the atomic mass of 207 g/mol.

Determining the optimum contact time

At this stage, five mg/l of the stock solution of each metal was separately prepared, and 100 milliliters of the mentioned amount was poured into 14 beakers. Afterwards, one gram of natural dolomite was added to seven beakers, and one gram of calcined dolomite was added to the other seven beakers for comparison. The weight of the contents was measured using the Sartorius AG (TE 124s) scale (made in Germany) with the precision of 0.0001.

Another solution was used as the control solution without adsorbent. The beakers were placed on an IKA HS/KS 260 control shaker at 150 rpm for the contact time of 5, 15, 30, 60, 90, and 180 minutes and removed at specific times. The experiments were conducted at the temperature of 20 ± 2 °C and initial pH of the solution. Following that, the solutions were filtered using filter papers and evaporated for 3-4 hours on hot plates (Hotplates Stuart CB 500, made in Germany) after separating the adsorbent. The measurements were carried out using an atomic absorption device (SpectrAA-

200Varian, made in the United States) using the evaporation technique.

Identifying the optimum adsorbent dosage

At this stage, 0.1, 0.5, 0.75, 1, 1.5, 2, and 5 grams of natural dolomite were added to seven out of the 14 beakers containing five mg/l of the stock solution of each heavy metal. In addition, 0.1, 0.5, 1, 0.75, 1.5, 2, and 5 grams of calcined dolomite were added to the other seven beakers for comparison. Furthermore, another solution was prepared as the control solution without adsorbent. The solutions were placed on the shaker for the mentioned optimum contact times, which were obtained for each metal in the previous step. The rest of the procedure was similar to the previous stage.

Determining the optimum concentration of the solution

After preparing the solutions at the stock solution concentrations of 1, 3, 5, 10, 20, and 50 mg/l for each heavy metal, the adsorbent dosage was calculated for each of the metals that were placed in six beakers containing 100 milliliters of the solution. Moreover, natural dolomite was added in equal amounts to the first six beakers, and calcined dolomite was added to the other six beakers at the same concentrations. A control solution was also prepared for each concentration. Afterwards, the solutions were placed on the shaker for the corresponding optimum contact times obtained in the first phase. The rest of the procedure was similar to the previous stage.

Identifying the optimum adsorption pH

At this stage, five mg/l of the stock solution of each heavy metal was prepared separately. Two beakers were selected for the pH of 6.5, each of which contained five mg/l of the prepared solutions. The optimum natural dolomite dosage was added to one beaker, while modified dolomite was added to the other beaker. Afterwards, the beakers were placed on the shaker at the optimum contact time calculated for each heavy metal, and the rest of the procedure was conducted similar to the previous stages. In addition, this experiment was repeated at the pH 7.5 and 8.5, and a solution

was used as the control. NaOH and H₂SO₄ were also used to adjust the pH using the CRIDON pH meter (Bsdic 20, made in Spain), which was calibrated prior to the experiments.

Results and Discussion

In this section, we have described the important influential factors in the adsorption of each heavy metal, including the contact time, pH, initial concentration of the solutions, and adsorbent dosage. In addition, the Langmuir and Freundlich isotherm models have been discussed.

Contact time analysis

The results of the experiments regarding the adsorption of five heavy metals onto natural and modified dolomite are depicted in Figures 1-5. In general, increased contact time was associated with the higher adsorption efficiency. As can be seen in the figure legends, the slope is extremely high, which could be attributed to the high concentration and multiplicity of the functional groups for the exchange of heavy metal ions at the outset of the reaction, which were easily available to the heavy metal ions.

According to the results regarding cadmium (Figure 1), increased contact time was associated with higher adsorption efficiency in both types of dolomite. With natural dolomite, the adsorption efficiency was observed to increase, followed by a reduction. However, in the case of modified dolomite, the adsorption efficiency increased with a higher slope.

In this phase, the highest removal efficiency of cadmium in was obtained using modified dolomite after 15 minutes (99%), while natural dolomite yielded the highest removal efficiency after 90 minutes (66%). Based on the results regarding calcined dolomite, the optimum contact time was considered to be 15 minutes.

The removal of zinc is depicted in Figure 2, indicating that the adsorption of zinc on natural dolomite increased, followed by a reduction over time, which could be attributed to the high concentration of zinc in the composition of this adsorbent. In other words, in the early contact times,

there were empty sites on the adsorbent surfaces for zinc adsorption, while the sites were gradually occupied, leading to the rejection of the metal by the adsorbent and decreased adsorption. However, more adsorption sites were observed using modified dolomite, reaching 96% within the first five minutes, followed by a state of balance (98%), and remaining constant after 60 minutes.

As for modified dolomite, the highest adsorption efficiency was obtained after three hours. As can be seen in Figure 3, the analysis of the equilibrium time for lead indicated that the adsorption occurred in two stages; initially, the metal was quickly adsorbed onto the adsorbent surface, and in the next step, mass transfer occurred slowly. However, as the sites were taken over time, the penetration of the heavy metal ions through the adsorbed ions and their adhesion to the empty spaces reduced the speed of adsorption. In this context, the highest efficiency for natural and modified dolomite within 15 minutes was estimated at 97% and 95%, respectively.

Nickel variations (concentration: 5 mg/l) and constant adsorbent dosage are illustrated in Figure 4. It could be argued that for a constant mass, the adsorption efficiency of nickel increased with modified dolomite, and the contact time was observed to increase as well. Therefore, after a specific period (i.e., equilibrium time), the adsorption efficiency reached its maximum and became constant. However, the results of the removal of nickel using natural dolomite were reversed; within the early minutes, the removal efficiency increased, followed by the significant decrease after approximately 20 minutes. This could be attributed to the high concentration of nickel in the dolomite structure. Due to the lack of adsorption sites, nickel was detached from the surface of natural dolomite, adversely affecting the solution and removal efficiency. The resulting

equilibrium time for nickel was estimated at 30 minutes.

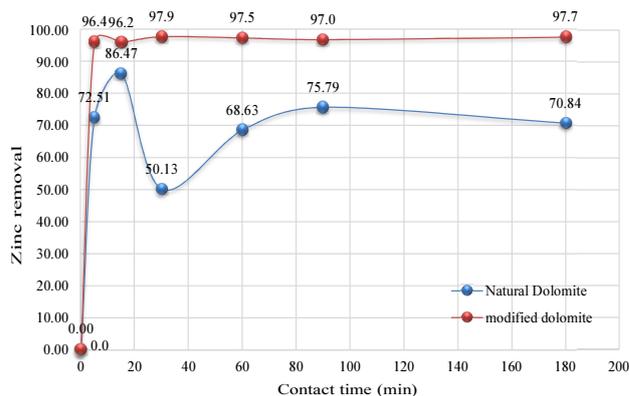


Fig. 1. Comparison of removal efficiency of zinc (%) from solution (5 mg/l) by natural dolomite and modified dolomite (1 g) within specified contact times

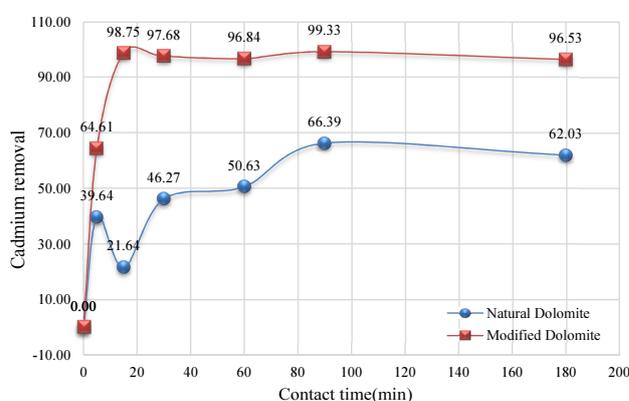


Fig. 2. Comparison of removal efficiency of cadmium (%) from solution (5 mg/l) by natural dolomite and modified dolomite (1 g) within specified contact times

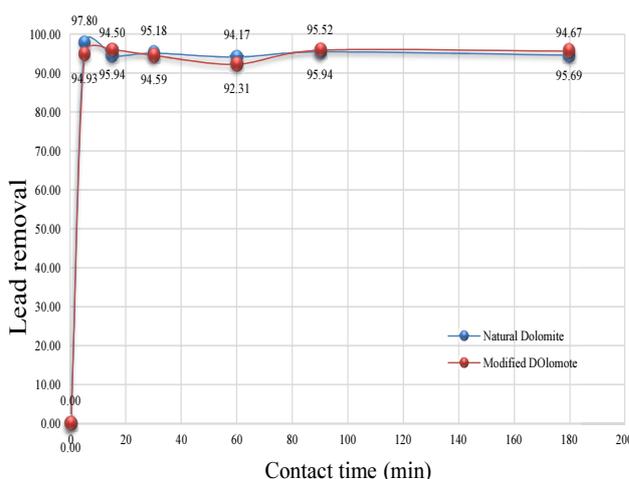


Fig. 3. Comparison of removal efficiency (%) of lead from solution (5 mg/l) by natural dolomite and modified dolomite (1 g) within specified contact times

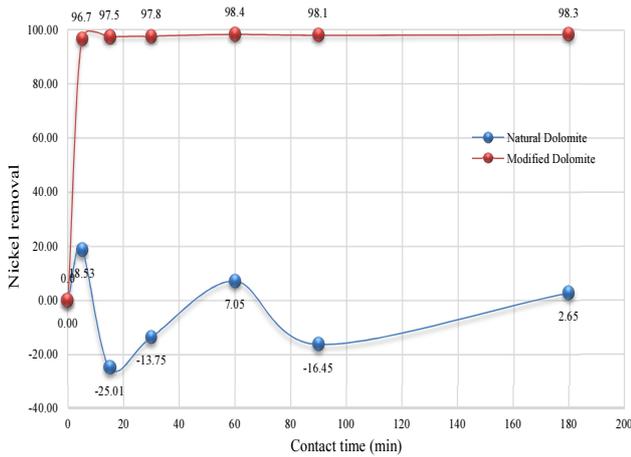


Fig. 4. Comparison of removal efficiency (%) of nickel from solution (5 mg/l) by natural dolomite and modified dolomite (1 g) within specified contact times

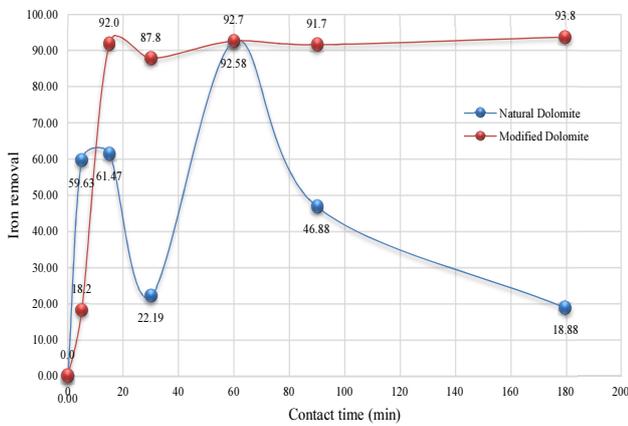


Fig. 5. Comparison of removal efficiency (%) of iron from solution (5 mg/l) by natural dolomite and modified dolomite (1 g) within specified contact times

According to the findings regarding the removal efficiency of iron (%) (Figure 5) relative to the contact time, modified dolomite could effectively increase with the contact time, reflecting the presence of several surface sites in modified dolomite. Furthermore, modified dolomite yielded the highest removal efficiency within 60 minutes (93%), reaching a state of equilibrium afterwards. With respect to natural dolomite, the removal efficiency increased at the outset of the contact times, followed by a reduction. However, the highest removal efficiency was obtained within 60 minutes (92%). Following that, the removal efficiency decreased with a high slope due to the

occupied sites and competition among the ions over adsorption.

Analysis of the effect of adsorbent dosage

In the second phase, the effect of the adsorbent dosage on the removal efficiency was assessed. In this phase, the increased amount of the adsorbent resulted in the significant increment of removal efficiency in both adsorbents. Natural dolomite showed no specific trend, while calcined dolomite increased with a specific trend. The growing trend was depicted at the outset of the diagram where it occurred more rapidly.

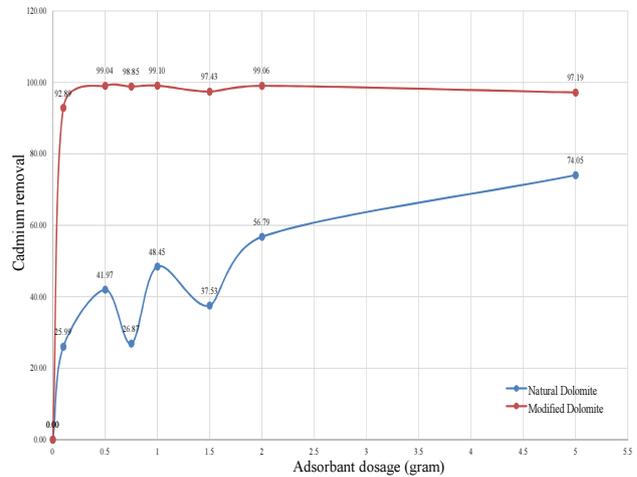


Fig. 6. Comparison of removal rate of cadmium from natural dolomite (5 mg/l) and modified dolomite with contact time of 15 minutes in specified adsorbents

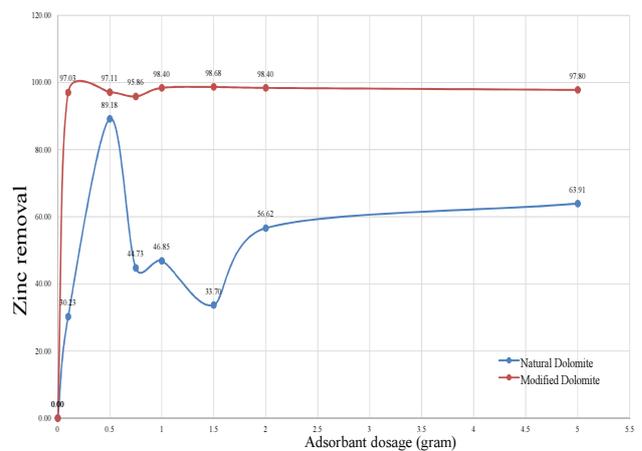


Fig. 7. Comparison of removal rate of zinc from natural dolomite (5 mg/l) and modified dolomite with contact time of 60 minutes in specified adsorbents

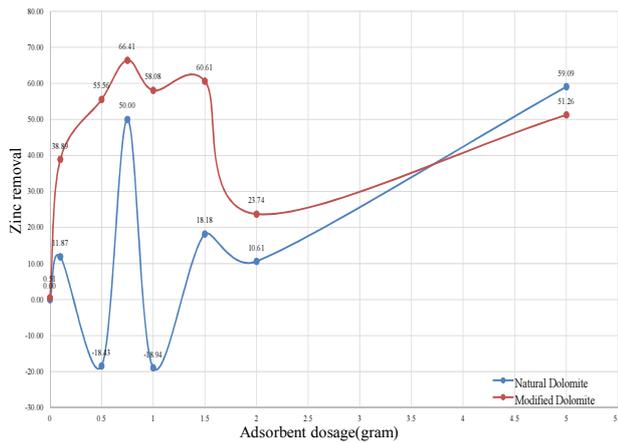


Fig. 8. Comparison of removal rate of lead from natural dolomite (5 mg/l) and modified dolomite with contact time of 15 minutes in specified adsorbents

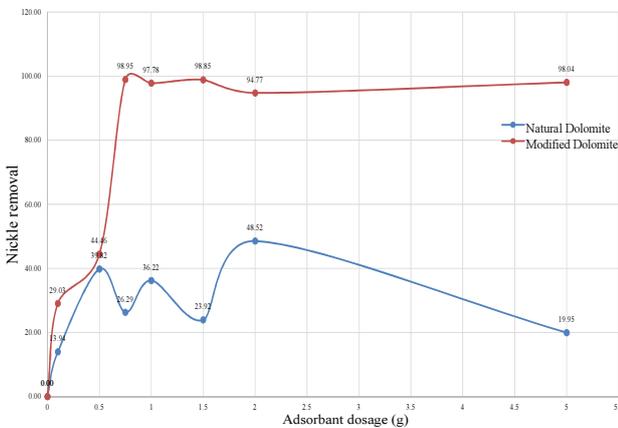


Fig. 9. Comparison of removal rate of nickel from natural dolomite (5 mg/l) and modified dolomite with contact time of 60 minutes in specified adsorbents

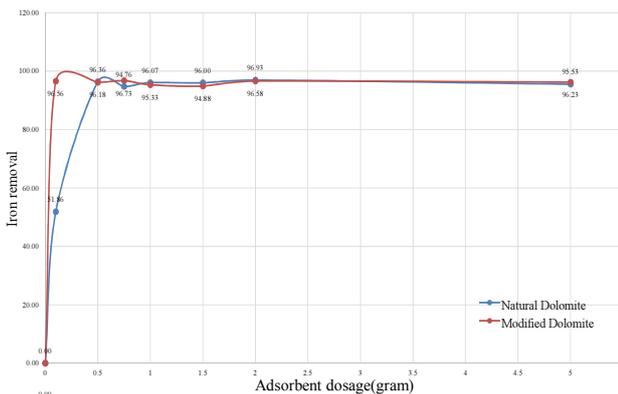


Fig. 10. Comparison of removal rate of iron from natural dolomite (5 mg/l) and modified dolomite with contact time of 60 minutes in specified adsorbents

According to the results obtained from the examination of cadmium (Figure 6), the increased adsorbent dosage escalated the removal efficiency due to the availability of the

surface area and presence of more adsorption sites.

The optimal dosage of the adsorbent for 0.5 g of cadmium and calcined dolomite was estimated at 74%, while it was determined to be 99% for five grams of cadmium and modified dolomite. Cost-effectiveness is an important determinant in the selection of the optimum adsorbent dosage. As is depicted in Figure 7, the removal efficiency of zinc was directly correlated with the adsorbent dosage for modified dolomite, while a fluctuation was observed in the case of natural dolomite. The highest adsorption of zinc (80%) occurred with 0.5 g of natural dolomite, while the highest removal efficiency with modified dolomite was approximately 97% with 0.1 g of modified dolomite.

According to the obtained results regarding the removal efficiency of lead (Figure 8) in terms of the adsorbent dosage, as the adsorbent dosage almost doubled, the surface pore areas, which are capable of adsorbing, doubled as well. As a result, the adsorption of lead was expected to double during this process. The highest removal efficiency obtained with 0.75 g of modified dolomite and one gram of natural dolomite was estimated at 67% and 50%, respectively. On the other hand, the results obtained for modified dolomite indicated no specific trend, and even two dosages were observed to have negative amounts due to the high concentration of lead in natural dolomite.

With respect to nickel (Figure 9), the increased adsorbent mass led to the reduction of the adsorption equilibrium time for two reasons. Firstly, the increased adsorbent mass was associated with the higher likelihood of collision between the solution elements and adsorption particles, thereby leading to an increment in the adsorption speed and reduced equilibrium time. Secondly, the increased adsorbent mass (or decreased solution concentration) caused the second phase of kinetic adsorption (i.e., formation of an adsorption-hindering boundary layer around the adsorbent) to lose its effect gradually, resulting in the increased adsorption speed and decreased equilibrium time. As can be seen in Figure 9, the with the increased modified

dolomite adsorbent, the curve ascended with a steep slope, reaching a state of equilibrium with 0.75 g of the adsorbent afterwards. The curve ascended and descended with an irregular trend for natural dolomite, suggesting that the increased adsorbent mass had no positive effect on the adsorption of natural dolomite.

With regard to iron (Figure 10), the increased adsorbent mass led to higher adsorption efficiency using natural and modified dolomite. Therefore, the adsorption efficiency obtained for 0.5 g of natural dolomite and 0.1 g of calcined dolomite was estimated at 94% and 96%, respectively, which indicated the tendency of dolomite for iron adsorption. However, the iron concentration in the dolomite structure was extremely low, thereby leading to lower desorption efficiency. With higher adsorbent masses, the adsorbent surface area was observed to increase, and more iron ions were adsorbed onto the adsorption surface.

Analysis of the effects of heavy metal concentrations

According to the analysis of cadmium (Figure 11), increasing the initial concentration of cadmium resulted in no specific trends with natural dolomite. In addition, the highest adsorption efficiency was observed within the range of 10-20 mg/l. As the concentration increased from 20 to 50 mg, the removal efficiency decreased drastically. However, this variation in the concentration was less effective in the case of calcined dolomite.

Concerning the use of modified dolomite for cadmium removal (Figure 11), the obtained results indicated that increasing the initial concentration of cadmium resulted in remarkable removal efficiency. Within the range of 1-5 mg, an increment was observed in the removal efficiencies, which subsided with a mild slope. As the concentration increased, the adsorption sites on the adsorbent surface were observed to decrease. In other words, the reduced concentration of the initial solution was associated with the decreased concentration of the heavy metal ions in the solution, and a large percentage of the ions were adsorbed onto the adsorbent. However, given the larger surface of

modified dolomite, this amount was found to be higher with modified dolomite.

According to the results of zinc removal by modified dolomite (Figure 12), increased concentration led to the initial reduction of removal efficiency, followed by a maximization (99%) at the concentration of 10 mg/l, and then it subsided. Therefore, it could be concluded that with the higher concentration of zinc ions in the solution, the removal time should be longer due to the decreased number of active sites on modified dolomite, which resulted in reduced adsorption sites.

With respect to natural dolomite, it could be concluded that the increased concentration led to the escalation of the removal efficiency, which subsided afterwards. This could be due to the fact that at lower concentrations, the competition over the adsorption was more intense, with the less possibility of removal. Consequently, the highest removal efficiency (36%) was obtained at the concentration of 5 mg/l. Moreover, as the concentration increased from 10 to 50 mg/l, natural dolomite negatively affected the removal efficiency.

The analysis of the lead concentrations (Figure 13) suggested that with modified dolomite, increasing the heavy metal concentration to 10 mg/l maximized the removal efficiency to 89%, while this rate declined afterwards. This trend was also observed with natural dolomite; in other words, at the concentration of 3 mg/l, the removal efficiency was 55%, which subsided afterwards.

With respect to the effect of concentration on the removal efficiency of nickel (Figure 14), it could be stated that the increased concentration of metal solution led to the reduced removal efficiency. On the other hand, the concentration of calcined dolomite within the range of 1-3 mg/l increased the efficiency, followed by a reduction and another increment. However, the concentrations of 10-20 mg/l significantly reduced the removal efficiency. As for natural dolomite, only the concentration of 5 mg/l was associated with a relatively successful removal efficiency, while at the other concentrations, nickel negatively affected the solution. This could be attributed to the presence

of nickel compounds in the structure of natural dolomite.

Analysis of the effect of the adsorbent concentration on iron removal efficiency (Figure 15) also revealed that the removal efficiency decreased at the low concentrations of both the adsorbents. The modified dolomite concentration of 5 mg/l was observed to have the highest efficiency (99%), while the natural dolomite concentration of 10 mg/l had the highest removal efficiency (92%). Following that, the removal efficiency decreased with a steep slope with both the adsorbents, reflecting the lack of adsorption capacity at higher concentrations.

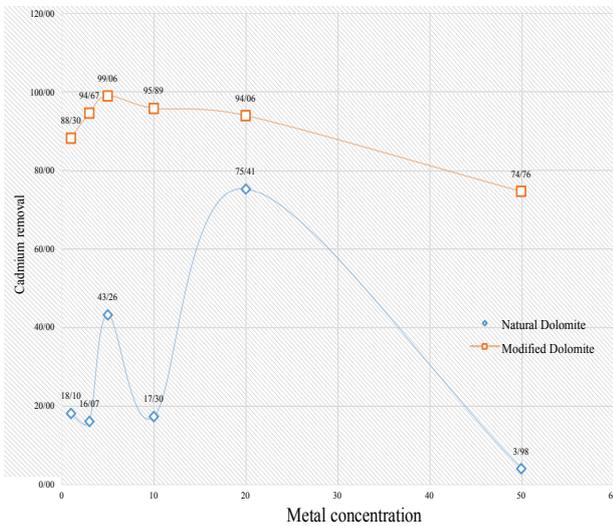


Fig. 11. Comparison of the removal percentage of cadmium from the solution for certain concentrations using natural and modified dolomite

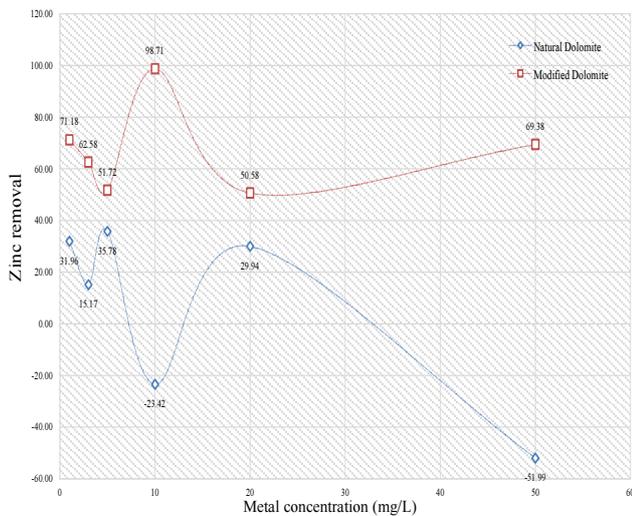


Fig. 12. Comparison of the removal percentage of zinc from the solution for certain concentrations using 0.1 g of natural and modified dolomite within a 60 minute contact time

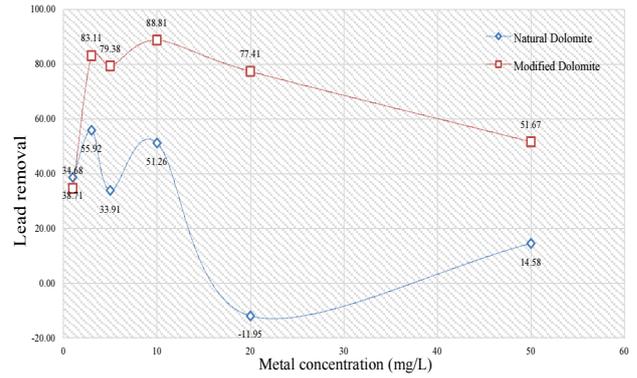


Fig. 13. Comparison of the removal of lead (%) from the solution in certain concentrations by 0.75 g of modified and natural dolomite within a 15 minute contact time

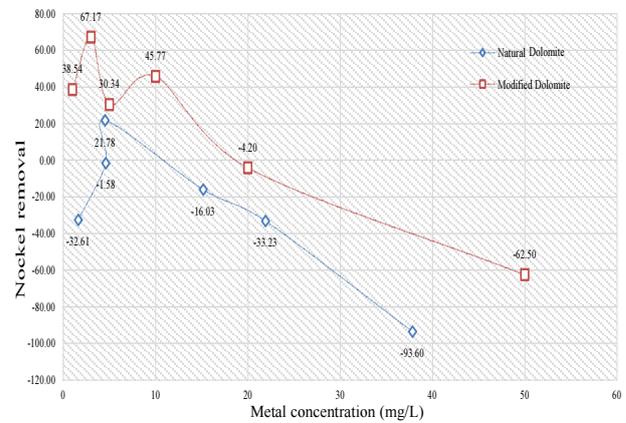


Fig. 14. Comparison of the removal of nickel (%) from the solution in certain concentrations by 0.75 g of modified and natural dolomite within a 30 minute contact

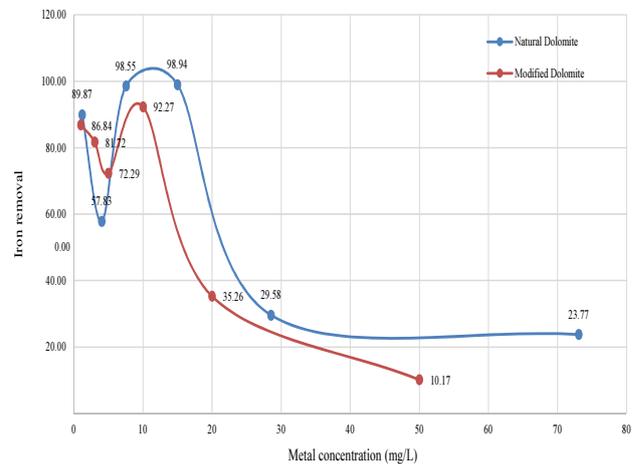


Fig. 15. Comparison of the removal of iron (%) from the solution in certain concentrations by 0.1 g of modified and natural dolomite within a 60 minute contact time

Analysis of the effect of optimum heavy metal pH

Evaluation of the effect of heavy metal pH on the efficiency of cadmium removal using natural

dolomite indicated that increased pH improved the removal efficiency with natural dolomite. Therefore, it could be stated that natural dolomite has better function in the removal of cadmium with alkaline pH, and the highest removal efficiency (81%) was obtained at the pH of 8.5. Moreover, the obtained results revealed that the removal of cadmium by modified dolomite at the pH of 6.5 led to the highest removal efficiency. However, as the pH increased to 7.5 and 8.5, the efficiency declined due to the higher pH rose, and cadmium adsorption decreased due to the release of hydroxide ions.

In the case of zinc, the adsorption rate was observed to decrease with both adsorbents at acidic pH. This could be due to the fact that lower pH is associated with the higher concentration of positive charges, which in turn resulted in electrostatic drifts and eventually reduced surface adsorption. On the other hand, increased pH was associated with reduced electrostatic drifts, leading to the decreased concentration of the positive charges on the adsorption sites, as well as the increased adsorption rate.

According to the results of the analysis, the

highest adsorption was observed with zinc at higher pH. In other words, at the pH of 8.5, the modified and natural adsorbents yielded the highest adsorption rates (81% and 68%, respectively).

Evaluation of the effect of pH on the removal efficiency of nickel indicated that the minimum efficiency for modified dolomite at the pH of 6.5 was 34%, which increased uniformly with pH. Consequently, at the pH of 8.5, the removal efficiency was maximized to 57%. At lower pH (i.e., acidic solutions), increased hydrogen ions were observed to increment the competition of H^+ with the solution cations, and H^+ was adsorbed onto dolomite instead of the heavy metal ions. Furthermore, the removal efficiency increased similarly with natural dolomite, with the exception that as the pH increased from 7.5 to 8.5, the removal efficiency declined. The reduction in the adsorption efficient at higher pH with natural dolomite could be attributed to the use of NaOH for pH adjustment. Based on Formula 1 (reaction), nickel bonds to OH^- and settles considerably, reducing the adsorption of nickel by natural dolomite.

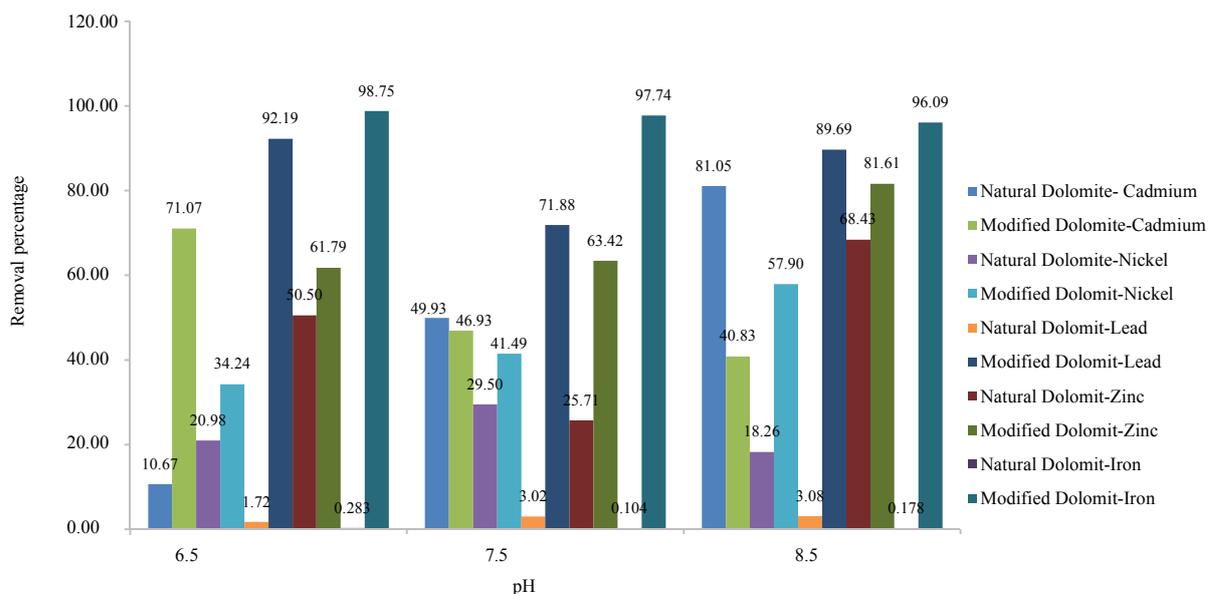
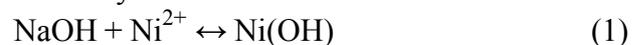


Fig. 16. Comparison of removal rate of heavy metals with optimum contact time and adsorbent dosage in 5 mg/l of solution and specific pH using natural and modified dolomite

Assessment of the effect of pH on the removal efficiency of iron indicated that with the increased pH, the removal efficiency escalated significantly with both the adsorbents. Therefore, the highest efficiency at the pH of 8.5 with natural dolomite and modified dolomite was estimated at 97% and 98%, respectively. On the other hand, the reduced removal of metal ions at low pH was caused by the high concentrations of H⁺ ions in the solution, which competed with the metal ions over the adsorption sites. As a result, the alkaline range suited the adsorption of iron.

According to the obtained results, increased pH led to the reduction of lead removal efficiency. As such, the highest removal efficiency with modified dolomite and natural dolomite at the pH of 6.5 was estimated at 93% and 74%, respectively, suggesting that the lead ions outperformed the hydrogen ions at acidic pH and were adsorbed onto the adsorbent.

Analysis of adsorption isotherms

Isotherms are the equations used in the state of equilibrium.¹⁸ The aim of adsorption isotherm calculation is to investigate the correlations between the amount of the adsorbent and level of adsorption during the process.¹⁹ In the current research, Langmuir and Freundlich models have been proposed separately for each heavy metal and adsorbent. Tables 1 and 2 show the results of the fitting of these models.

The Langmuir adsorption isotherm is used more commonly compared to other adsorption isotherms. In this model, it is assumed that the adsorption regions on the adsorbent surface are

uniform and have the same adsorption capacity. The Langmuir isotherm could be noted, as follows:²⁰

$$\frac{1}{q_e} = \frac{1}{ab} \cdot \frac{1}{C_e} + \frac{1}{b} \tag{2}$$

where C_e is the adsorbent concentration in the state of equilibrium in the liquid phase (mg/L), q_e represents the adsorbent ion amount in the state of equilibrium (mg/g), a is a constant that depends on the continuity of the adsorption sites and adsorption energy (L/mg), and b denotes the maximum of an adsorbed heavy metal ion to complete a layer (a constant depending on the adsorption capacity; mg/g). Moreover, the $1/q_e$ versus $1/C_e$ curve is a straight line with a slope of $1/ab$ and a y-intercept of $1/b$. As such, a and b could be calculated.

In 1926, Freundlich studied the adsorption of substances onto charcoal, proposing the following experimental model of adsorption onto an adsorbent:²¹

$$\log q_e = \frac{1}{n} \log C_e + \log k \tag{3}$$

where n and k represent the Freundlich model constants, denoting the adsorption capacity and intensity of adsorption, respectively.

The Langmuir and Freundlich isotherms for heavy metals are presented in Tables 1 and 2. The Langmuir model has been developed for single-layer adsorption with the assumption that the adsorbent surface has sites with equal energies, and each adsorptive molecule is assigned to a specific site. As a result, it probably reflects the uniform distribution of the active sites onto the adsorbent surface.

Table 1. Results of fitting langmuir and freundlich models for natural dolomite and each heavy meta

Metal ion	Isotherm Langmuir			Isotherm Freundlich		
	R ²	a	B	R ²	n	K
Cadmium	0.0045	-2.99	0.49	0.007	0.90	2.42
Nickel	0.03	35.67	-0.24	0.15	-32.25	1.12
Zinc	0/00005	-121	4.32	0.02	-5.74	6.82
Iron	0.123	0.16	357.14	0.17	5.98	5.23
Lead	0.10	-0.14	1.31	0.173	3.29	1.66

Table 2. Results of fitting freundlich and langmuir models for modified dolomite and each heavy metal

Metal ion	Isotherm Langmuir			Isotherm Freundlich		
	R ²	a	B	R ²	n	K
Cadmium	0.992	0.044	22.72	0.73	1.43	16.98
Nickel	0.65	-4.85	0.0723	0.65	-9.09	2.404
Zinc	0.75	500	12500	0.33	2.52	38.10
Iron	0.96	142.8	0.014	0.027	3.40	44.66
Lead	0.35	0.711	2.27	0.57	1.16	3.90

The Freundlich coefficient (n) must be within the range of 1-10 in order for satisfactory adsorption. The Langmuir and Freundlich isotherms for cadmium are depicted in Tables 1 and 2.

According to the results regarding cadmium removal with natural dolomite, the correlation-coefficients of the experimental data based on the Freundlich model ($R^2=0.004$) were higher compared to the Langmuir correlation-coefficients, which confirmed the higher conformity of the data to the Freundlich model. As for modified dolomite, the data were in compliance with the Langmuir isotherm ($R=0.99$). The Langmuir model has been developed for single-layer adsorption with the assumption that the adsorbent surface has sites with equal energies, and each adsorptive molecule is assigned to a specific site. Therefore, it probably reflects the uniform distribution of the active sites onto the adsorbent surface.

With regard to the removal of nickel, the correlation-coefficients of the experimental data for natural dolomite and Freundlich model were higher compared to the Langmuir correlation-coefficients ($R^2=0.0302$), reflecting the higher conformity of the data to the Freundlich model. As for modified dolomite, the data were in compliance with the Langmuir isotherm ($R^2=0.654$).

The Freundlich and Langmuir isotherms for zinc are presented in Tables 1 and 2. According to the obtained results regarding zinc removal, the correlation-coefficients of the experimental data with natural dolomite and the Langmuir model ($R^2=0.751$) were higher compared to the Freundlich correlation-coefficients, reflecting the higher conformity of the data to the Langmuir model. As for modified

dolomite, the data were in compliance with the Freundlich isotherm ($R^2=0.33$).

With respect to the removal of iron, the correlation-coefficients of the experimental data with natural dolomite and the Freundlich model ($R^2=0.27$) were higher compared to the Langmuir correlation-coefficients, reflecting the higher conformity of the data to the Langmuir model. As for modified dolomite, the data were in compliance with the Langmuir isotherm ($R^2=0.9$).

The obtained results regarding the removal of lead indicated that the correlation-coefficients of the experimental data for natural dolomite and the Freundlich model ($R^2=0.173$) were higher compared to the correlation-coefficients of the Langmuir model, indicating the higher conformity of the data to the Langmuir model. As for modified dolomite, the data were in compliance with the Freundlich isotherm ($R^2=0.5$).

Most of the studies regarding calcite are in remarkable agreement in terms of the observations on the kinetics of sorption processes, denoting an initial rapid uptake of the trace metal, followed by a period of relatively slow removal from the solution. These phenomena were also evident in the present study.²²

Conclusion

The present study aimed to evaluate the removal of nickel, cadmium, lead, iron, and zinc using natural and thermally-modified dolomite based on functional parameters, including pH, contact time, heavy metal concentrations, and adsorption level. According to the results of the analysis of contact time, the shortest optimum time for the removal of the mentioned heavy metals was obtained with modified dolomite.

The optimum contact times for cadmium, lead, zinc, iron, and nickel were estimated at 15, 15, 60, 60, and 30 minutes, respectively. Furthermore, the highest removal efficiency was observed in cadmium at the initial pH, while the removal efficiency of zinc increased with the pH escalating from 6.5 to 8.5.

The highest efficiency was obtained with the initial pH of the solution (99%) as observed in the high efficiency of iron at the pH of 8.5 (97-98%). However, the removal efficiency of lead reduced with increased pH. In addition, iron, nickel, and zinc showed the highest removal efficiency at the pH of 8.5, while iron yielded a higher level of removal efficiency compared to the other two metals (98%). Therefore, the effective removal range for cadmium and lead was the acidic range.

In the analysis of the adsorption isotherms of nickel, iron, and cadmium using modified dolomite, the data matched the Langmuir model, while they were in compliance with the Freundlich models in the case of lead and zinc; these models were identified as the optimum models with the use of natural dolomite. On the other hand, thermally-modified dolomite exhibited extremely higher adsorption efficiency for heavy metal cations in water compared to natural dolomite. Therefore, dolomite has attracted the attention of researchers due to its simplicity and cost-efficiency compared to the costly resins used for ion removal. The current research could lay the groundwork for a series of investigations regarding the removal of heavy metals from water and effluents through an economical process.

Acknowledgements

Hereby, we extend our gratitude to the Rural Water and Wastewater Company of Tehran Province (Iran) and the Iranian Refractories Procurement and Production Company for the financial support of this study. We would also like to thank the managers of these companies for assisting us in this research project.

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