Removal of Ni and Zn heavy metal ions from industrial waste waters using modified slag of electric arc furnace

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Abstract

In the present study modified slag of electric arc furnace which itself is considered as an industrial waste material was used to eliminate nickel and zinc metals from industrial waste water. The modified slag was characterized by SEM, XRD and XRF analyses and it was demonstrated that it could be used as an efficient novel adsorbent. Experimental and thermodynamic evaluations of heavy metal removal efficiency were carried out at different conditions including temperatures of 25, 35 and 50°C. In addition, in order to develop this process on an industrial scale, optimization of different parameters such as contact time, metallic ion concentration, adsorbent amount, adsorbent particle size, temperature, pH, etc was carried out. Results showed that the optimum conditions for removal of nickel and zinc ions were at the adsorbent dosage of 30 mg L⁻¹, adsorbent particles size finer than 75 μm and adsorption time of 3 h. Moreover, by increasing the process temperature, the adsorbing efficiency was improved. Kinetic investigations displayed that the adsorption of metallic ions was more likely correlated with the pseudo-first-order model than the pseudo-second-order model and diffusion model. Additionally, the correlation coefficient indicated that the Freundlich adsorption model predicted more precisely than that of the Langmuir model for adsorption of nickel and zinc metallic ions.

1. Introduction

Industrial wastewaters containing heavy metals and insertion of them into the environment is one of the most important concerns of the industries [1, 2]. For this reason, proper solutions for the economic and efficient removal of heavy metals from industrial waste waters are vital. At present, the application of low-cost and natural materials as adsorbents is getting to attention due to the simple adsorption process [3–5]. Metals such as mercury, chromium, lead, zinc, copper, nickel, arsenic, cobalt, etc are considered toxic heavy metals [6, 7]. Acidic wastewaters containing ions of the aforementioned heavy metals are usually byproducts of metal coating, mining and pigment industries which are harmful to the environment [8].

Different methods including adsorption, chemical precipitation, ion exchange, membrane filtration, immersion agglomeration are employed for removing heavy metals from aqueous solutions [8, 9]. Lately, the use of low-cost materials e.g. lime stone, olivine, slag, zeolite, leonardite, modified and non-modified bauxite, fruit peels and palm oil for adsorption of heavy metal ions is highlighted [8, 10, 11].

Steel slag discharged from the blast furnace, electric arc furnace, converter furnace is a byproduct of the steel making process which is produced on large scale and considered as a waste material so far. It is very detrimental to the environment and composed of different oxides including CaO, SiO₂, FeO, Al₂O₃, MgO and various alkaline materials that can be hydrated by H₂O and release OH⁻ ion. Based on previous reports steel slag was used...
as an adsorbent for the elimination of phosphate, ammonia, organic contaminations, and heavy metallic ions (copper, arsenic, lead, manganese, chromium, Ni and Zn) [8, 9, 12, 13].

In this investigation, by using low-cost electric arc furnace slag and application of proper heat treatment, a novel high-efficiency adsorbent for removal of heavy Ni and Zn metal ions was prepared. For this purpose, the physical and chemical properties of slag were characterized. Then adsorption kinetics correlations and adsorption isotherm models were surveyed and the optimum conditions for adsorption were studied. This study aimed to remove Ni (II) and Zn (II) heavy metallic ions from aqueous solutions by modified slag. The operational parameters of contact time, adsorbent particle size, metallic ion concentration, pH and temperatures were surveyed and their optimum values were determined. Moreover, the kinetics and mechanism of the adsorption process were studied.

2. Materials and methods

2.1. Materials

The materials used in this study include Ni and Zn metallic elements, which were obtained from Merck, Germany in addition to granulated slag of electric arc furnace with the size ranging from 0.1 to 3 mm.

2.2. Slag processing

To increase the specific surface and activity of the slag, first any contamination such as soil, etc was removed from the slag. Then it was washed with distilled water and dried. Finally, heat treatment was performed to increase its surface activity because it has low activity; i.e. use of slag as heavy metal adsorbent requires structural modification. Heat treatment was performed to increase the porosity and remove the volatile materials as well as to stabilize the crystalline phases. Since the transformation of the unsteady phases to thermally-stable phases is an exothermic process, the temperature of the heat treatment should be elevated high enough to provide the conditions for removal of the volatile phases and change the phase, and on the other hand it should not be so high that glass phases are formed and the porosity is reduced. The heat treatment was carried out at 600 °C for 2 h to change the phase. At this stage, the beta tricalcium silicate phase is converted into the gamma tri-calcium silicate phase. Also After that, the slag particles were ground with a jar mill for 48 h so that the size of the particles reaches below 1 mm. Finally, the slag particles were reached to under 75 μm by planetary ball mill.

2.3. Preparation of simulated wastewater

At first, a solution with 1000 mg l⁻¹ concentration was prepared. Then, the concentration declined to 20 mg l⁻¹ to optimize the parameters. Hydrochloric acid was used to dissolve Ni and Zn. The slag powder was then mixed with the solution by a stirrer at the temperatures of 35 and 50 °C and by a jar mill at 25 °C for 0, 5, 30, 180 and 540 min. A centrifuge device was used to remove the slag particles from the solution.

Various speeds were applied to optimize the stirring speed. For the jar mill the agitation speed was 90 rpm while it was 150 rpm and 250 rpm for the stirrer at different temperatures. To study the effect of pH, solutions with different initial pHs were prepared and adjusted by HCl. The concentrations of metal ion in solutions were selected as 20, 40 and 80 mg l⁻¹. According to the statistical discussion of available surface area for the adsorbent, it was first selected as 30 g l⁻¹, and then it was evaluated for 20 and 50 g l⁻¹ dosages. To examine the effect of particle size, particles with sizes of 75 μm < x < 1 mm and x < 75 μm were employed.

2.4. Characterization

In order to determine the present phases in the slag, an x-ray diffraction (XRD) machine (Philips model PW3040, Netherlands) was utilized with a wavelength of CuKα (λ = 1.5405 Å) was used. Scanning electron microscopy (SEM) (LEO model 435VP, Netherlands) was used to study the microstructure of the adsorbent. The samples were coated with gold to obtain conductivity. To measure the concentration after adsorption, atomic absorption spectroscopy (AAS) was utilized after the solutions were placed in the adsorption bath. Moreover, to ensure the accuracy and precision of the obtained data, the calibration of AAS was checked after analyzing every five experiments and three replicates of each sample were carried out.

2.5. Adsorption kinetics

The study to adsorption kinetics of the modified slag of electric arc furnace the experiments were carried out with contact time of 5, 30, 180 and 540 min at pH = 5, T = 25 °C, initial metallic ion concentration of 20 mg l⁻¹ and adsorbent dosage of 30 g l⁻¹ in a volume of 200 ml. The amount of adsorbed heavy metal ion (qₜ)(mg g⁻¹) at t time was calculated based on equation (1):
where, \( C_0 \) and \( C_e \) are the initial and final concentration of metallic ion at t time, respectively, V is volume and \( m \) is the weight of the used adsorbent. The equivalent concentration of metallic ions \( (q_e) \) was calculated by equation (2):

\[
q_e = \left( \frac{C_0 - C_e}{V} \right) m
\]

where, \( C_0 \) (mg l\(^{-1}\)) and \( C_e \) (mg l\(^{-1}\)) are the initial and equivalent concentrations of metallic ions, respectively. The kinetic data of 3 h contact time for the modified slag were correlated with kinetic models of pseudo-first-order model (equation (3)), pseudo-second-order (equation (4)), and diffusion model (equation (5)).

\[
\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

\[
q_t = k_3 t^{0.5} + c
\]

where, \( q_e \) (mg g\(^{-1}\)) and \( q_t \) (mg g\(^{-1}\)) are adsorption capacities of the adsorbent at equilibrium and t time (t), respectively. \( k_1, k_2 \) and \( k_3 \) are the coefficients of pseudo-first-order, pseudo-second-order, and diffusion equations, respectively. In the pseudo-first-order model, the kinetic parameters are obtained from the

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**Figure 1.** (a) SEM micrograph and (b) BET graph of the modified slag.

**Figure 2.** XRD pattern of modified slag.
log \((q_e - q_t)\) versus \(t\) graph. While, in the pseudo-second-order model, the kinetic parameters are obtained from the \(t/q_e\) versus \(t\) graph. Moreover, in the diffusion model, the parameters are attained from \(q_t\) versus \(t^{0.5}\).

### 3. Results and discussion

#### 3.1. Slag characterization

The SEM micrograph of the modified slag is shown in figure 1 (a). As it can be seen, the slag particles have an irregular and randomized morphology, which indicates the active sites for removal of Ni and Zn metallic ions. By modification of the slag, parameters such as the specific surface, the total volume of open porosity, the volume of microporosity, and mesoporosity were increased significantly, which contributes to the adsorption of metallic ions present in the aqueous solution. The high specific surface of modified slag compared in comparison with unmodified slag is resulted from the opening of the canals, dragging of the diaphragm diameter and microscopic reactions [8]. The elemental analysis of the slag is presented in table 1. Regarding the chemical composition of the slag, it can be seen that the chemical composition of slag, it can be found that slag had basic

| XRF elemental analysis | SiO\(_2\) | CaO | Al\(_2\)O\(_3\) | FeO | MgO | SO\(_3\) | MnO | P\(_2\)O\(_5\) | NO\(_2\) | Cl |
|------------------------|---------|-----|----------------|-----|-----|---------|-----|-------------|--------|---|
| wt. %                  | 13.9    | 23  | 3.3            | 42.4| 13.6| 0.55    | ≥1  | ≥1          | ≥1     | — |

BET specific surface = 33.10 cm\(^2\) g\(^{-1}\), density = 3.28 g cm\(^{-3}\).
property, thus it can exchange ions and adsorb Ni and Zn ions. Additionally, the iron oxide in the slag can adsorb the cations such as arsenic and chromium plus the anions such as phosphorus. In addition, calcium hydroxide increases the pH of the solution and causes the deposition of cations [11]. In figure 2, the x-ray diffraction pattern of the slag is demonstrated. As it is displayed, the slag had several phases including wustite, magnetite, calcium iron oxide and silicon calcium oxide. The main phases of the slag with amounts higher than 10 wt.% were Ca$_2$SiO$_4$, Ca$_3$SiO$_5$, FeO and Ca-Mg-Mn-Zn-Fe$_2$O$_4$ compound [14, 15]. The adsorption capacity of the adsorbent increased by alkaline modification via heat-treating the slag. According to the results, sodium hydroxide had a good effect on slag modification. By heating the slag at 800 °C for 1 h, the optimum conditions for increasing the adsorption capacity were obtained [16]. The slag of the steelmaking process includes magnesia, titania, Na$_2$O and MnO. The specific surface of the slag of converter furnace and alumina catalyst are 2.10 and 153.545 m$^2$ g$^{-1}$, respectively. However, during the calcination process at 900 °C, the specific surface areas of the slag of the convertor furnace and alumina catalyst reduced to 0.8 and 56.56 m$^2$ g$^{-1}$, respectively, and thus a portion of the structural porosity was eliminated at high temperatures [14]. The XRD pattern reveals that a major portion of the slag consisted of the crystalline phase (figure 2). In addition, the analysis of the compounds showed that phases of wustite (FeO), larnite ($\beta$-Ca$_2$SiO$_4$), brownmillerite (Ca$_2$(Al,Fe)$_2$O$_5$), lime (CaO) and magnetite (Fe$_3$O$_4$) were present in the milled slag. Figure 1(b) depicted the BET graph of the slag. The adsorption and desorption curves of these samples can be seen in the figure. The obtained curves are of type IV isotherm and their hysteresis is of the second type (H2 according to IUPAC classification), which indicates the presence of layered mesopores in the synthesized compounds. The specific surface area obtained for the powder was about 28.19 square meters per gram and the average pore size was 20 nanometers.

Figure 4. The elemental map analyses of the modified slag used as the adsorbent after the adsorption process.
Figures 3 and 4 demonstrates the SEM micrographs and elemental map analysis of the adsorbent before and after the adsorption process, which confirmed the presence of metallic ions on the surface of the adsorbent and proper removal of the Zn$^{(II)}$ and Ni$^{(II)}$ ions. Moreover, the EDS results before the modification were in good agreement with the results of the XRF technique.

Figures 5, 6. The effect of contact time on the adsorption of nickel and zinc metallic ions. (a) the pseudo-first-order model, (b) the pseudo-second-order model and (c) the diffusion model for the adsorption of nickel and zinc metallic ions.

Figures 3 and 4 demonstrates the SEM micrographs and elemental map analysis of the adsorbent before and after the adsorption process, which confirmed the presence of metallic ions on the surface of the adsorbent and proper removal of the Zn (II) and Ni (II) ions. Moreover, the EDS results before the modification were in good agreement with the results of the XRF technique.
the total adsorbed ions. For Ni adsorption of Ni and Zn metallic ions. As can be observed in changes of adsorption with time signifi-
cantly declined after 3 h contact time, which was the optimum time for adsorption of Ni and Zn metallic ions. As can be observed in figure 5, after 3 h no significant change was seen in the total adsorbed ions. For Ni (II) and Zn (II) ions the final removal efficiencies of 96.3% and 99.8% were obtained, respectively. At the initial times, Ni ions were more adsorbed than Zn. On the other hand, with increasing the contact time, the adsorption of Zn ions washigher than Ni ions. The initial rate of adsorption obtained, respectively. At the initial times, Ni ions were more adsorbed than Zn. On the other hand, with increasing the contact time, the adsorption rate became constant, which indicates the occupation of available adsorption sites. Thus, the prediction of this adsorption model is based on chemical adsorption.

Furthermore, table 2 shows a comparison between the results of this study and earlier investigations. As can be seen, significant improvement was achieved using the novel modified slag-based adsorbent. Base on table 2, the studies reporting high adsorption efficiencies either have long contact times, or uses high doses of adsorbent materials. Any of the mentioned parameters causes the prolonged processing time or contamination of the aqueous solution by the adsorbent material. Nevertheless, some investigations, which report adsorbents with high efficiencies focus only on a single type of heavy metallic ions. However, the rest of the studies report efficiency values lower than that of the current study.

In table 3 and figure 6, the kinetic data for pseudo-first-order, pseudo-second-order and diffusion models are presented. According to the correlation coefficient of R^2, the pseudo-second-order model offered a higher correlation coefficient in comparison with pseudo-first-order and diffusion models. The adsorption kinetics of the pseudo-second-order equation is based on the adsorption capacity in the solid phase and emphasis on the number of adsorption active sites. Thus, the prediction of this adsorption model is based on chemical adsorption.

| Adsorbents                        | Heavy metal | pH | Initial pH | Adsorbent dosage | Contact time | Tem. | The highest removal efficiency | References |
|-----------------------------------|-------------|----|------------|------------------|--------------|------|-------------------------------|------------|
| Steelmaking slag                  | Zn (II)     | 7  | —          | 1.6 mg l^-1      | 179 d        | —    | 99.3%                         | [21]       |
| Biomass                           | Ni (II)     | 3  | —          | 10 g l^-1        | 30 min       | 301  | 68%                           | [22]       |
| Landfill leachates                | Ni (II)     | 8  | —          | 10 g l^-1        | 24 h         | —    | 32%                           | [3]        |
| LD slag                           | Ni (II)     | 7.9| 9          | 2 g l^-1         | 24 h         | 318 K| 85.29 mg g^-1                | [23]       |
| geopolymer                        | Ni (II)     | 7.9| 9          | 2 g l^-1         | 24 h         | 318 K| 14.72 mg g^-1                | [23]       |
| Blast Furnace Slag                | Ni (II)     | 9  | 9          | 10^{-6}–10^{-3} M| 4 h          | 333  | 55.76 mg g^-1                | [24]       |
| Natural bentonite                 | Ni (II)     | 8  | —          | 1 g l^-1         | 24 h         | 298  | 50 mg g^-1                   | [25]       |
| Washed bentonite                  | Ni (II)     | 8  | —          | 1 g l^-1         | 24 h         | 298  | 20 mg g^-1                   | [25]       |
| Calcined bentonite                | Ni (II)     | 8  | —          | 1 g l^-1         | 24 h         | 298  | 22 mg g^-1                   | [25]       |
| Zeolite                           | Ni (II)     | —  | —          | 0.5 g l^{-1}     | 24 h         | —    | 1.98 mg g^{-1}               | [26]       |
| Steel slag                        | Zn (II)     | 7  | —          | 25 g l^-1        | 1 h          | —    | 96.79%                        | [27]       |

Table 2. A comparison between the results of this study and earlier investigations.

| Metallic ion | Pseudo-first-order model | Pseudo-second-order model | Diffusion model |
|--------------|--------------------------|----------------------------|-----------------|
|              | K_1                      | R^2                        | K_1            | R^2          | K_1        | R^2            |
| Ni           | 0.00023                  | 0.9996                     | 0.029          | 1            | 0.00057    | 0.9693        |
| Zn           | 0.00046                  | 0.9806                     | 0.032          | 0.999        | 0.00092    | 0.8996        |

3.2. Adsorption kinetics

3.2.1. Effect of contact time

It is evident in figure 5 that as it was expected, by increasing the contact time, the adsorption increased, but the changes of adsorption with time significantly declined after 3 h contact time, which was the optimum time for adsorption of Ni and Zn metallic ions. As can be observed in figure 5, after 3 h no significant change was seen in the total adsorbed ions. For Ni (II) and Zn (II) ions the final removal efficiencies of 96.3% and 99.8% were obtained, respectively. At the initial times, Ni ions were more adsorbed than Zn. On the other hand, with increasing the contact time, the adsorption of Zn ions washigher than Ni ions. The initial rate of adsorption depends on the available adsorption sites. By increasing the contact time up to 3 h, the slope of the adsorption curve was high, but after this time the adsorption rate became constant, which indicates the occupation of available adsorption sites. At high concentrations of metallic ion in the solution, the effect of contact time is more significant and more important than the effect of contact time in lower concentration solutions. As shown in figure 5, by increasing the time, the removal rate of the metallic ion increased, but in the early stages, the rate of Ni and Zn ions elimination was so much higher, which can be due to the presence of available active sites for adsorption [9, 17–20]. Also, by elevating the concentration of metallic ions in the solution, the diffusion of metallic ions in the silicate structure decreased and subsequently the amount of Ni and Zn ions lowered [11]. Furthermore, table 2 shows a comparison between the results of this study and earlier investigations. As can be seen, significant improvement was achieved using the novel modified slag-based adsorbent. Base on table 2, the studies reporting high adsorption efficiencies either have long contact times, or uses high doses of adsorbent materials. Any of the mentioned parameters causes the prolonged processing time or contamination of the aqueous solution by the adsorbent material. Nevertheless, some investigations, which report adsorbents with high efficiencies focus only on a single type of heavy metallic ions. However, the rest of the studies report efficiency values lower than that of the current study.

In table 3 and figure 6, the kinetic data for pseudo-first-order, pseudo-second-order and diffusion models are presented. According to the correlation coefficient of R^2, the pseudo-second-order model offered a higher correlation coefficient in comparison with pseudo-first-order and diffusion models. The adsorption kinetics of the pseudo-second-order equation is based on the adsorption capacity in the solid phase and emphasis on the number of adsorption active sites. Thus, the prediction of this adsorption model is based on chemical adsorption [8, 9, 12]. Studies have shown that by increasing the pH of the solution, the constant of the pseudo-first-order equation increases, which is related to the existing compounds in the slag [28, 29].
3.2.2. Effect of pH

In figure 7, the effect of pH variation on the removal percentage of Ni and Zn ions is displayed. As the initial pH of the solution increased, the adsorption of Ni and Zn ions increased. This increased the ion exchange on the surface of the adsorbent. Moreover, with increasing pH, the desirable conditions for the deposition of metallic ions are provided. As a result of the ion exchange and precipitation process, the metallic ions were removed from the wastewater. Ni ion adsorption mechanism involves the formation of a nickel hydroxide ($\text{Ni(OH)}_2$) complex in heterogeneous nucleus sites at the surface of the slag. Ni cannot replace the calcium sites, so it forms a hydroxide layer. The desirable pH for adsorption of $\text{H}_2\text{PO}_4^-$ is 6.61, while it is 8.75 for adsorption of $\text{NH}_4^+$. It should be noted that in low calcia contents, $\text{NH}_4^+$ ion adsorption is limited. In previous studies [14], it has been reported that the release of calcium ions in the solution occurs with increasing pH. This leads to the coagulation of anionic molecules due to the electrostatic adsorption between the anions and the positive charges at the slag surface. The most effective adsorption capacity was at pH = 2. However, when pH is higher than 2, the adsorption process continues. In acidic pH, a high electrostatic attraction occurs between the positive charge of the slag surface and the heavy metal ions [30]. The final stability of pH in a wide range is related to two processes: (I) hydrolysis of the compounds at the surface of slag that leads to the release of $\text{OH}^-$ ions, (II) the accumulation of $\text{OH}^-$ ions of the adsorbed metallic ions. If the adsorption is assumed to occur at the surface of $2\text{CaO}.\text{SiO}_2$, the hydrolysis reaction of the surface in an ideal state would be in the form of reactions 1–3.
In order to model pH conditions and predict the performance of the adsorbent, various solutions with acidic, neutral, and alkaline properties can be considered hypothetically. For instance, by decreasing the pH, since it does not pass the pH limitation for deposition of metallic ions, the ion exchange process takes place in these conditions, the adsorption process is carried out and the deposition of heavy metallic ions does not occur. When the slag is inserted into the solution, the active compounds present in the slag are hydrated as the following reaction.

In acidic solutions:

\[
\text{Si} + \text{OH} \rightarrow \text{H} \rightarrow \text{O} \rightarrow \text{H}[\text{Me} \text{(OH)}_2]^2 \leftrightarrow \text{Si} \rightarrow \text{OMe} + \text{H}_2\text{O}^+ \tag{R1}
\]

In neutral solutions:

\[
m\text{CaSiO}_3\text{H}_2\text{SiO}_3^- + \text{MeOH}^+ \leftrightarrow m\text{CaSiO}_3\text{MeSiO}_3 + \text{H}_2\text{O} \tag{R2}
\]

In alkaline solutions:

\[
m\text{CaSiO}_3\text{H}_2\text{SiO}_3^- + \text{Me(OH)}_2 \leftrightarrow m\text{CaSiO}_3\text{MeSiO}_3 + \text{H}_2\text{O} + \text{OH}^- \tag{R3}
\]
Me(OH)$_2$ cannot precipitate on the solid surfaces, because when these reactions occur, this is converted into MeSiO$_3$ in the solution [24].

3.2.3. Effect of particle size
Figure 8 shows the effect of particle size on the removal of Ni and Zn ions. By reducing the size of the adsorbent particles the adsorption of metallic ions is enhanced. Because the smaller the size of the slag particles is, the more active sites are provided for adsorption that results in better physical adsorption. As shown in the SEM micrographs, particles with a size below 75 $\mu$m had better adsorption behavior. As the size of the particles improves, the diffusion path increases and as a result, the adsorption reduces. The smaller the particle size is, the greater the rate of internal diffusion and mass transfer are. Therefore, the diffusion of material into the adsorbent improves [30, 31].

3.2.4. Effect of adsorbent dosage
Figure 9 shows the effect of the adsorbent dosage on adsorption of Ni and Zn ions. The dosages of 20, 30, and 50 g L$^{-1}$ were used to evaluate the adsorbent dosage effect on adsorption. By rising the amount of adsorbent, the adsorption increased due to greater available sites for ion exchange and higher basicity of the solution. However, it should be noted that the amount of adsorbent should be optimized to avoid high costs. The optimum amount of adsorbent in this study was obtained to be 30 g L$^{-1}$. The initial rate of adsorption is related to the number of available sites. By increasing the adsorbent dosage, available sites are not saturated so the adsorption increased [27, 30, 31].

3.2.5. Effect of the metallic ions initial concentration
Figure 10 illustrates the effect of the initial concentration of metallic ions in the solution on the removal of Ni and Zn ions. The initial concentration is an important factor in the adsorption process. By improving the initial concentration of metallic ions the adsorption rate increased. The optimum adsorption of metallic ions in this study was carried out with a 50 mg l$^{-1}$ adsorbent dosage. It was observed that with elevating the initial concentration of heavy metallic ions from 20 to 80 mg l$^{-1}$, the amount of adsorption increased. An increase of adsorption capacity at high initial concentrations can be attributed to increased mobility. At pH = 5, the surface of the adsorbent is negatively charged, resulting in an electrostatic repulsion in contact with Ni and Zn ions. When the initial concentration increases, the diffusion rate of the metallic ions to the adsorbent surface increases with a greater potential difference and more intense electrostatic adsorption, i.e. more metallic ions are adsorbed on the solid surface. However, in the process of adsorption, by the occupation of active sites, a decrease in the efficiency of metallic ions removal was observed. In low concentrations of Ni and Zn ions, due to the great number of active contact sites on the surface of the adsorbent, metallic ions can be easily adsorbed. When the initial concentrations of Ni and Zn ions increased, more exchange sites are occupied and saturated and consequently metallic ions cannot be adsorbed. Thus, after a while, the rate of adsorption efficiency became constant. The initial concentration of metallic ions is the driving force for adsorption, hence the high initial concentration of metallic ions increases the rate of adsorption. At the onset of the process, an increase in the
concentration of metallic ions had a strong effect on the adsorption process, but in the progress, adsorption declined [9, 13, 18, 32].

3.2.6. Effect of stirring speed

Figure 11 shows the effect of stirring speed on the adsorption percentage of Ni and Zn ions. By elevating the stirring speed turbulence increases and subsequently as the slag reacts more with the solution, which increases the physical adsorption. The magnetic stirrer was used at speeds of 150 and 250 rpm, and the jar mill was used at a speed of 90 rpm. In experiments performed by the jar mill, results were superior to that of the magnetic stirrer, because the mixing condition and the agitation state of the jar mill provide better turbulence. As the stirring speed improved, the diffusion coefficient and mass transfer increased in the solution. As a result, the resistance of the aqueous body to the diffusion was removed. When the stirring speed was reduced, other parameters of resistance to diffusion were dominated by the adsorption process [27].

3.2.7. Effect of temperature

Figure 12 shows the effect of temperature on the adsorption of Ni and Zn metal ions. As was expected by increasing the temperature, adsorption improved. Because atomic mobility has a direct relationship with temperature. As the temperature of the slag increases, the slag has a stronger pozzolanic effect, so coagulation of the slag particles occurred. It should be mentioned that as the temperature rises, there is a possibility of adsorption decrease. As the temperature elevated above 60 °C, due to alkaline activation, the rate of adsorption increased that is partly because of the alkaline activity of the slag. The main product of the alkaline activation of the slag is calcium silicate hydrate with aluminum in the structure of the C-A-S-H gel or (C-CaO; A-Al2O3; S-SiO2; H-H2O) [33]. The trend of adsorption increases up to 50 °C temperature and after that the variation is reduced. The chemical composition of the slag in the adsorption process is remarkable. In the case of acidic solutions, silica performs the adsorption process. While for alkaline solutions, calcia performs the adsorption. Additionally, for neutral solutions iron oxide and alumina carry out the process. The principle of the Ni adsorption mechanism is the ligand exchange from cation with calcium dissolution in the C-A-S-F composition and Ni deposition.

\[
S - OH + Ni^{2+} \rightarrow S - ONi + H^+ \quad & \quad Ca - S + Ni^{2+} \rightarrow Ni - S + Ca^{2+}
\]

(S = adsorbent)

Calcium deposition is accomplished by dissolution of calcium from C-A-S-F and targeting the anions in the solution.

\[
CaHPO_4 \downarrow . Ca_3(PO_4)_2OH \downarrow . Ca_3(PO_4)_2 \downarrow
\]

Also, adsorption of the C-A-S-F adsorbent with the hydroxyl group is similar to adsorption of iron oxide, silica and NH4+ at the surface of alumina, FeOMgO and MgFe2O4 [14].

Figure 12. Effect of temperature on the adsorption of nickel and zinc ions.
3.3. Adsorption models

Isotherm models for the adsorption of Ni and Zn ions using modified slag are presented in Figure 13. Langmuir, Freundlich, and hybrid isotherm models are shown in equations 6–8:

\[
\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m}
\]

(6)

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

(7)

\[
q_e = \frac{q_m K_f C_e}{1 + (K_f C_e)^{1/n}}
\]

(8)

where \(C_e\) (mg l\(^{-1}\)) is the concentration of metallic ions, \(q_e\) (mg g\(^{-1}\)) is the equilibrium adsorption capacity, \(q_m\) is the maximum adsorption capacity of adsorbent, and \(b\) (L mg\(^{-1}\)) is Langmuir adsorption constant and related to

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Figure 13. Adsorption isotherms for nickel and zinc: (a) Langmuir (25°C), (b) Freundlich (25°C), (c) Langmuir (35°C), (d) Freundlich (35°C), (e) Langmuir (50°C) and (f) Freundlich (50°C).
adsorption energy. $K_f$ and $n$ are Freundlich equilibrium constant, i.e. adsorption intensity and adsorption capacity, respectively. $C_e$ (mg/dm$^3$) is the adsorbent equilibrium concentration, while $k_T$ and $m_T$ (dm$^3$ g$^{-1}$) are constants. Langmuir adsorption process is homogeneous and monolayer. The calculated parameters of Freundlich and Langmuir symmetric models are presented in table 4. Figure 13 reveals the isotherm graphs of Langmuir and Freundlich adsorption models. Regarding the correlation coefficient ($R^2$), the Freundlich isotherm model is more accurate for the adsorption of both Ni and Zn ions. In the Langmuir model, it is assumed that adsorption occurs at homogeneous regions of the adsorbent, and it essentially coincides with monolayer adsorption. By increasing the temperature increases, free energy increases. High adsorption at elevated temperatures is attributed to the dragging of the pores and activation of available sites. As a result, it can be said that the process of adsorption is exothermic. As the temperature rises, the interface of the adsorbent and the solution is more closely linked and organized, so that entropy changes increase [6, 8, 9, 30, 31]. In tables 4 and 5, the variables of the Freundlich and Langmuir models, and the thermodynamic parameters of Freundlich and Langmuir models are brought, respectively. Figure 14 shows ln $b$ versus $1/T$ diagram for removal of Ni and Zn ions using modified slag of electric arc furnace.

Table 4. Thermodynamic variables for the adsorption process.

| Metallic ion | T($^°$C) | $R^2$ | $k_f$ | $N$ | $q_m$ | $R^2$ | $b$ |
|-------------|----------|------|------|----|------|------|----|
| Ni          | 25       | 0.999| 1.783| 0.00061| 0.617| 0.989| 1.153|
|             | 35       | 0.993| 1.949| 1.00068| 0.742| 0.992| 2.910|
|             | 50       | 0.98 | 2.0034| 1.00078| 0.186| 0.975| 9.815|
| Zn          | 25       | 0.891| 1.36 | 0.75690| 0.492| 0.953| 1.340|
|             | 35       | 0.98 | 1.63016| 1.0002 | 0.630| 0.869| 2.407|
|             | 50       | 0.967| 1.79000| 1.11200| 0.142| 0.968| 14.600|

Table 5. Thermodynamic variables for the Freundlich and Langmuir models.

| T ($^°$C) | Metallic ion | Ln $b$ | $\Delta G$ $\left( \frac{1}{mol} \right)$ |
|-----------|--------------|--------|---------------------------------|
| 25        | Ni           | 0.142  | 352.725                         |
|           | Zn           | 0.292  | 725.110                         |
| 35        | Ni           | 1.068  | 2735.232                        |
|           | Zn           | 0.815  | 2241.823                        |
| 50        | Ni           | 2.280  | 6134.899                        |
|           | Zn           | 2.681  | 7199.163                        |
To investigate the acceptance of the adsorption process, a non-dimensional parameter called the separation factor ($R_L$) was used which was calculated according to equation 9. The values of $R_L$ were between 0 and 1 for both metallic ions and they decreased by increasing the concentration that indicates the acceptance of both processes. Figures 15(a) and (b) shows the diagram of the concentration versus $R_L$ for Ni and Zn ions at different temperatures, respectively.

$$R_L = \frac{1}{1 + bC_0}$$ (9)

4. Conclusions

The present investigation demonstrated that applying heat treatment on the steel slag of electric arc furnace slag changed its structure and the milling process increased the specific surface of the slag. These modified slag particles showed proper efficiency for the removal of Ni and Zn heavy metal ions. Despite the high alkaline property of the modified slag, it is a suitable option for the elimination of Ni and Zn ions. Different parameters of pH and particle size had a significant effect on the removal of metallic ions. Because these two factors play an important role in the adsorption status (chemical adsorption or physical adsorption). By increasing the pH and/or reducing the particle size, the adsorption increased. According to the obtained results, there may be different mechanisms for the adsorption of heavy metal ions. Electrostatic adsorption of metallic ions is one of the factors that can be particularly effective because with increasing the pH of the solution, the adsorption is accelerated. The surface of the slag sample is negatively charged, thus by increasing the pH of the solution, the electrostatic adsorption capacity of positive ions enhances. On the other hand, it was observed that the metal ions were adsorbed even at low pH values (acidic solutions). Therefore, it could not be said that there was only one mechanism involved in the adsorption. Thus, other mechanisms such as physical adsorption or ion exchange mechanism were active especially for the adsorption of zinc ions because at acidic pH values, zinc ions were also significantly removed. At acidic pH values, the ion exchange potential increases, so this mechanism is one of the most likely mechanisms to remove zinc ions. The optimum parameters for the adsorbent were particle size below 75 μm, the initial pH of 8 for the solution, an adsorbent dosage of 30 g L⁻¹, 3 h of contact time, and a temperature of 50 °C. Modeling studies showed that the Freundlich isotherm and pseudo-second-order equation had the best correlation with experimental results of Ni and Zn ions adsorption. Thermodynamic evaluations displayed that by increasing the temperature adsorption of the heavy metal ions by the modified slag improved.

Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.
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