Removal of nickel and methylene blue from aqueous solutions by steel slag as a low cost adsorbent

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Abstract:

Nowadays, wastewater from various industries contains a large number of harmful heavy metals and coloring agents, which have to be removed to restore the quality of the environment. In this study, the removal of nickel ions (Ni^{2+}) and methylene blue (MB) from the aqueous solution using steel slag as a low cost adsorbent was investigated. The chemical and mineralogical compositions, as well as the surface area of slag, were analyzed by using X-ray fluorescence spectroscopy, X-ray diffraction, and the Brunauer-Emmett-Teller method (BET). The effect of several important parameters such as contact time, adsorbent dose, pH, temperature, and initial adsorbate concentration on the adsorption process was studied systematically by batch experiments. The adsorption data were well correlated with the Langmuir isotherm model by all samples. The maximum adsorption capacity of the raw slag samples was 36.49 mg/g for Ni^{2+} and increased from 0.68 to 1.98 mg/g for MB after being acid-activated. The determined thermodynamic parameters indicate that the adsorption of Ni^{2+} and MB on steel slag is spontaneous in nature, endothermic (for Ni^{2+}), and exothermic (for MB).

Keywords: ***adsorption, dye, heavy metals, low cost adsorbent, steel slag, water treatment.***

Classification number: ***2.2***

Introduction

It is well known that water is a precious and irreplaceable resource for human and animals' life [1]. However, water pollution of heavy metals and dyes, which are major contributors to the contamination of water streams, has been a serious environmental problem in the recent years. The increasing water contamination by heavy metal ions and dyes has become a significant concern for ecological systems and public health because of their nonbiodegradable property, bioaccumulation, and toxicity, even at low concentrations [2]. Nickel is one of the important toxic heavy metals that is widely used in electroplating, printing, storage-battery industries, silver refineries, and production of some alloys. High concentration of nickel causes poisoning effects like lung, nose, bone cancers, headaches, dizziness, nausea, cyanosis, and extreme weakness [3]. One of the high consuming materials in the dye industry is MB, which is the most commonly used substance for dying cotton, wool, and silk [4]. The MB can cause eye burns, nausea, vomiting, diarrhea, dyspnea, tachycardia, cyanosis, methemoglobinemia, and convulsions if inhaled [5, 6]. Therefore, the treatment of effluent, containing heavy metal ions, and dyes such as nickel and MB, is necessary due to their harmful effects on humans.

Among the various methods currently applied for removing heavy metals and dyes from the water industry, adsorption is the most widely used method due to its merits of efficiency, economy, and simple operation [7]. Different adsorbents have been used for the removal of MB and nickel ions from aqueous solutions, including graphene [8, 9], bentonite [10], activated carbon [4], perlite [11], pumice [12], and hydroxyapatite [13, 14]. However, these adsorbents are relatively expensive, and this has restricted their application at times.

Steel slag is the main by-product of the iron and steel industry. A huge amount of it is accumulated in the environment and causes numerous ecological problems. Therefore, determining the sustainable usage of accumulated steel slag for other purposes will bring economic and environmental benefits. In the recent years, steel slag has been reported as potential adsorbent to remove pollutants from waste water [15-19]. In this study, steel slag was chosen as a low cost adsorbent to remove nickel ions and methylen blue dye. The main objective of this work was to evaluate the removal ability of steel slag and its activated form for Ni^{2+} and MB under different experimental conditions.

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Materials and methods

Materials and chemicals

The experiment material used in this study was electric arc furnace (EAF) steel slag obtained from a steelmaking plant (Danang, Vietnam). The collected steel slag was crushed and sieved to obtain particles. Activated slag was obtained by soaking raw crushed steel slag with 2 M HCl for 24 hours at room temperature. After that, the acid suspension was filtered by vacuum filter and then, the residue was washed with distilled water. Finally, the sample was dried at 100°C for 12 hours and ground to a powder state. Nickel sulfate hexahydrate and methylen blue were purchased from Merck. The reagents dimethylglyoxime (99.00%), NaOH (99.95%), and HCl (36.5%) were provided by Sigma Aldrich. All other reagents used in this study were analytical grade, and distilled or double distilled water was used in the preparation of all solutions.

Characterization of adsorbent

The chemical composition of the slag was determined by X-ray fluorescence spectroscopy (XRF) using a Philips PW 2404 instrument. The morphologies of the samples were investigated by scanning electron microscopy (SEM, Hitachi S4800). The mineralogical composition was analyzed by an X-ray diffractometer Rigaku Ultima IV (Japan), operating at 45 kV and 40 mA, using Cu-Kα radiation of $\lambda = 0.15418$ nm, 2θ ranging from 5 to 60°, and step size 0.1°. Phase identification was carried out by comparing the peak positions of the diffraction patterns with ICDD (JCPDS) standards. Surface area of the slag was measured by the BET on Micromeretics TriStar 3000 instrument.

Batch studies

Batch adsorption studies were performed at different doses of adsorbent, initial pH, contact time, concentrations of Ni^{2+} and MB. For each experiments, three replicates of the adsorbents (0.5 g) were mixed with 50 ml solutions of Ni^{2+}/MB in 150 ml conical flasks at different initial concentrations and a certain temperature. The pH of the solutions was adjusted by adding 0.1 M aqueous solutions of NaOH or HCl using a pH meter InoLab Multi 9310. To ensure homogeneous mixing, an orbital shaker with an agitation speed of 150 rpm was used throughout the experiment. Then, the samples were centrifuged at 5000 rpm for 10 min. The concentrations of the nickel ions and the MB dye before and after adsorption were estimated using an UV-visible spectrophotometer (UV-VIS Ultrospec 8000). The effect of the adsorbent dose was conducted using 2.5-20 g/l of adsorbent. The effect of pH was investigated over a pH range of 2-8. The effect of contact time was studied under different given contact time between 5 min and 120 min.

The percentage removal (R%) and the amount of adsorbed nickel ion and MB dye were calculated using the following equations:

$$R = \frac{C_o - C_e}{C_o} \cdot 100 \qquad (1)$$

$$Q_e = \frac{(C_o - C_e).V}{m} \qquad (2)$$

where: C_o and C_e are the initial and final concentrations of Ni^{2+} ions and MB before and after the adsorption in aqueous solution (mg/l); Q_e is the amount of Ni^{2+} and MB dye adsorbed by the slag (mg/g); V is the volume of solution (l); m is the mass of adsorbent (g).

Results and discussions

Characterization of sorbent

The chemical and physical characteristics of the steel slag are presented in Table 1. The result showed that the steel slag of this study mainly contains calcium, iron, silicon, magnesium, aluminum, manganese, and phosphorus compounds. The joint presence of calcium oxide and alumina silicate compounds could facilitate the provision of negatively charged sites for cation exchange reactions with metal ions in the aqueous solution [20]. The surface area and density of the steel slag are 4.23 m^2/g and 3.025 g/cm^3, respectively. Aqueous suspensions of the slag have a high pH value (10.52) because of great content of calcium hydroxide (30.23 w%) and basic oxides in it, which lead to a high capacity of the slag to neutralize strong acidic media.

The mineralogical compositions of slag samples were determined by the XRD analysis, and obtained results are given in Fig. 1. The analysis of the diffraction patterns showed that both slag samples are heterogeneous materials consisting the following major crystalline phases: larnite (Ca_2SiO_4), wuestite (FeO), gehlentite ($Ca_2Al(AlSiO_7)$), mullite ($3Al_2O_3.2SiO_2$), and quartz (SiO_2). Other minor constituent phases in the analyzed samples are very difficult to identify because of the complexity of the diffractograms. Additionally, XRD patterns show that the peaks of the activated slag are more intense and clearer compared to the raw steel slag. This may be because some impurities in the raw slag have been removed when it was soaked in the acid solution.

Morphology study

Figure 2 shows the morphologies of the slag samples before and after adsorption, as characterized by SEM. It can be seen from the SEM images that there is no significant change in morphology of the slag samples before and after adsorption of Ni^{2+} and MB. Under SEM, the slag particles showed irregular shapes with sharp edges about 0.5 µm to 2 µm in size.

Effect of initial solution pH

The initial pH value of the adsorbate solution is one of the most important factors influencing the adsorption process due to its strong effect on the surface charge, the surface binding sites of the adsorbent, and the degree of ionization and species of adsorbate [21]. The effect of initial pH on the adsorption process was studied in the range from 2 to 8 at 25±2°C, the adsorbent dosage of 0.5 g, contact time of 60 min, 50 ml

Table 1. The chemical and physical characteristics of the slag.

Chemical composition (w%)							BET surface area (m²/g)	Density (g/cm³)	pH
CaO	*Fe_2O_3*	*SiO_2*	*Al_2O_3*	*MnO*	*MgO*	*P_2O_5*			
30.23	28.57	22.19	6.68	4.17	2.39	2.20	4.23	3.025	10.52

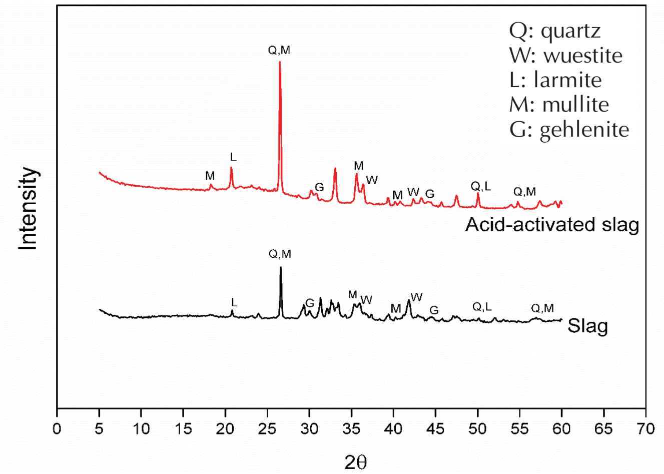

Fig. 1. XRD patterns of slag samples.

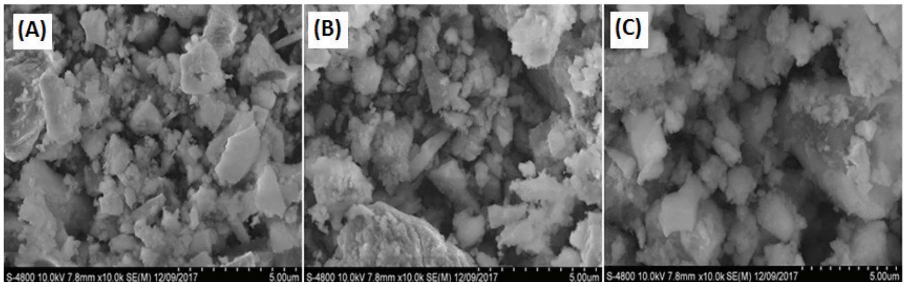

Fig. 2. SEM images of slag samples: (A) before adsorption, (B) after Ni^{2+} adsorption, and (C) after MB adsorption.

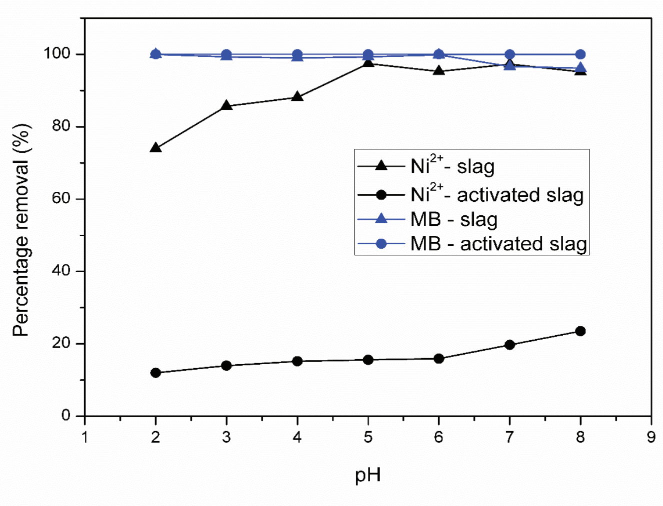

Fig. 3. Effect of pH on Ni^{2+} and MB adsorption onto slags.

of initial Ni^{2+} and MB solutions with a concentration of 200 mg/l and 5 mg/l, respectively. Fig. 3 shows the effect of the initial pH on the adsorption of Ni^{2+} ions and MB onto different forms of slag. It can be seen that the MB removal percentage of both slag samples had no significant change and reached 99.9% for the activated slag sample at the whole pH range. While the raw slag can remove 98.6-99.9% of MB from the aqueous solution at pH 2-6 and its removal ability insignificantly decreased to 96.1% at pH 7-8. For Ni^{2+}, the percentage removal generally increased with increasing the pH of the solution. It can reach 77.5% at pH 2 and increase to 98.3% at the pH range of 5 to 8 for raw slag sample. The removal percentage of Ni^{2+} by activated slag in the range of pH 2-8 was 12.3-23.5%, which is about 4-5 times lower than that by raw slag. This can be due to the decreased alkalinity of the slag when it was activated by acid. Therefore, the experiments of nickel adsorption onto the activated slag were not conducted any further.

At a lower pH than 5.0, the Ni^{2+} ion adsorption capacity of slag was low due to the increased concentration of hydronium (H_3O^+) ions, which compete for Ni^{2+} binding sites on the slag surface. The increase in pH resulted in a reduction in H_3O^+ ions; the adsorption sites were available to be occupied by more Ni^{2+} ions than H_3O^+ ions. At an alkaline pH, there was hydroxyl group abundance on the slag surface, which promoted the adsorption of metal cations. However, at pH values higher than 7.0, precipitation usually occurs simultaneously between Ni^{2+} ions and hydroxide ions, and could lead to inaccurate interpretation of adsorption [22]. Based on the above results, the optimum pH values of 5.0 and 6.0 were selected for the adsorption study regarding the removal of Ni^{2+} and MB dye, respectively.

Effect of equilibrium time

The determination of the contact time between adsorbent and adsorbate required for the system to reach equilibrium is important to determine the possible discrimination order in the behavior of the slag for Ni^{2+} and MB dye removal. The effect of contact time on adsorption of Ni^{2+} and MB onto slag samples was carried out at different contact times ranging from 5 min to 120 min at 25±2°C, adsorbent dosage of 0.5 g, the selected optimum pH values, and 50 ml of adsorbate solutions (200 mg/l for Ni^{2+} and 5 mg/l for MB). As shown in Fig. 4, over 97% of Ni^{2+} ions and MB was adsorbed on the slag phase after only 10 min of the equilibrium periods. The adsorption of the Ni^{2+} and MB dye by the raw slag exhibits a similar trend. The percentage removal increased with a lapse of contact time, and equilibrium was reached after 30 min. Moreover, it can be seen that the adsorption of Ni^{2+} and dye on raw slag had taken place in two stages where the first stage is faster than the second stage. This phenomenon can be confirmed by the slope of adsorption line which had value in the first step of the adsorption process higher than the second. The initial rapid stage can be associated with the presence of the large number of binding sites at exterior surface, which are being fully available at the initial stage of adsorption process. When the exterior adsorption sites become filled with adsorbates, the adsorbate ions then moved with slow rate from the exterior to the interior.

The adsorption of MB on activated slag occurred relatively quickly because there were more active sites on the surface compared to the nonactivated slag. The amount of MB dye removed by the activated slag also rose up to more than 99% after 5 min, and remained invariable until the adsorption attained a balanced status.

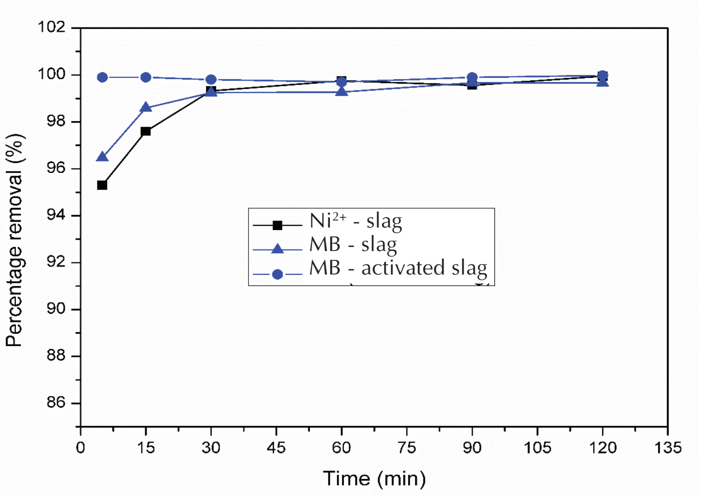

Fig. 4. Effect of contact time on adsorption of nickel and MB onto slag.

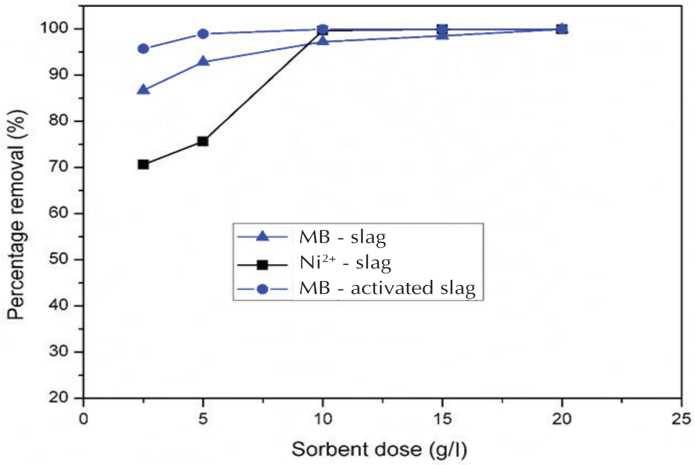

Fig. 5. Effect of sorbent dose on adsorption of Ni^{2+} and MB onto slag.

Effect of adsorbent dose

To select the best-required dose for the scale-up and to design large-scale equipments, the effect of adsorbent dose on MB dye and Ni^{2+} removal was investigated. The effect of the dose on the adsorption was studied by varying the amount of adsorbent from 0.25 to 1 g in 50 ml of adsorbate solutions with initial concentrations of 200 mg/l (for Ni^{2+}) and 5 mg/l (for MB) at a room temperature of 25°C, optimum pH, and a contact time of 30 min. The relationship between the removal percentage of Ni^{2+} ions and MB and the adsorbent dose is shown in Fig. 5.

It is shown that the removal efficiency of Ni^{2+} ions and MB increased with increasing the adsorbent dose for all the slag samples due to the availability of more surface area on the adsorbent. This means that there was a small surface area for the attachment of the adsorbate ions at a low adsorbent dose, resulting in the low efficiency of Ni^{2+} ions and MB removal. However, as the adsorbent amount increased, more sites became available for the attachment; hence, the removal capacity of the adsorbent increased. The increase in the slag dose from 2.5 to 5 g/l resulted in an increase in the adsorption of Ni^{2+} from 70.6 to 75.7% and of MB from 86.7 to 92.8% for the raw slag samples and from 95.7 to 98.9% for the activated slag samples. When the adsorbent dose was sufficient (> 10 g/l), over 99% of adsorbates could be removed. Thus, the complete removal was possible with an adsorbent dose of 10 g/l.

Effect of initial concentration

The effect of the initial concentration on the removal efficiency and adsorption capacity of Ni^{2+} ions and MB on the slag samples at room temperature of 25°C, an adsorbent dose of 10 g/l, optimum pH, and contact time of 30 min is shown in Fig. 6.

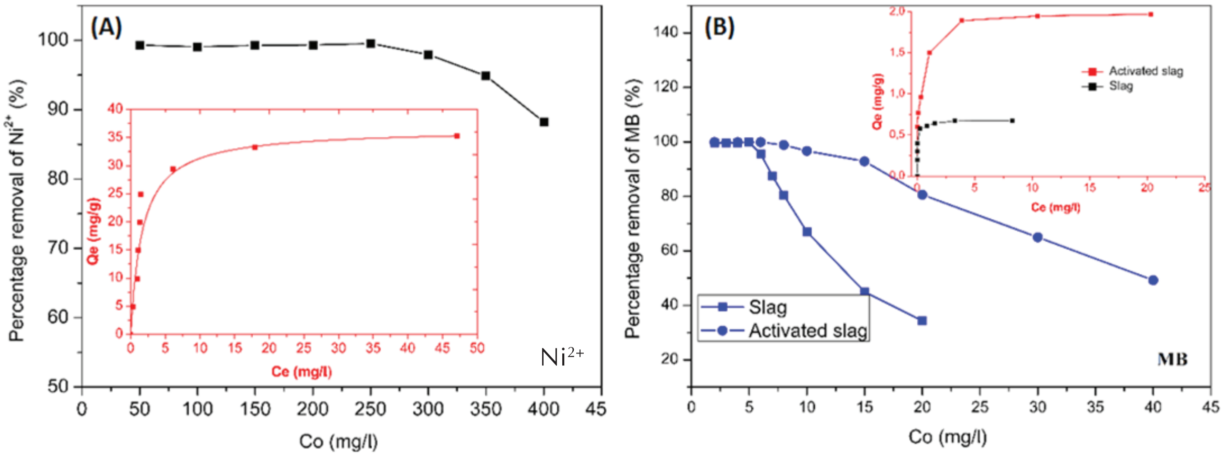

Fig. 6. Effect of initial concentration on (A) Ni^{2+} and (B) MB adsorption.

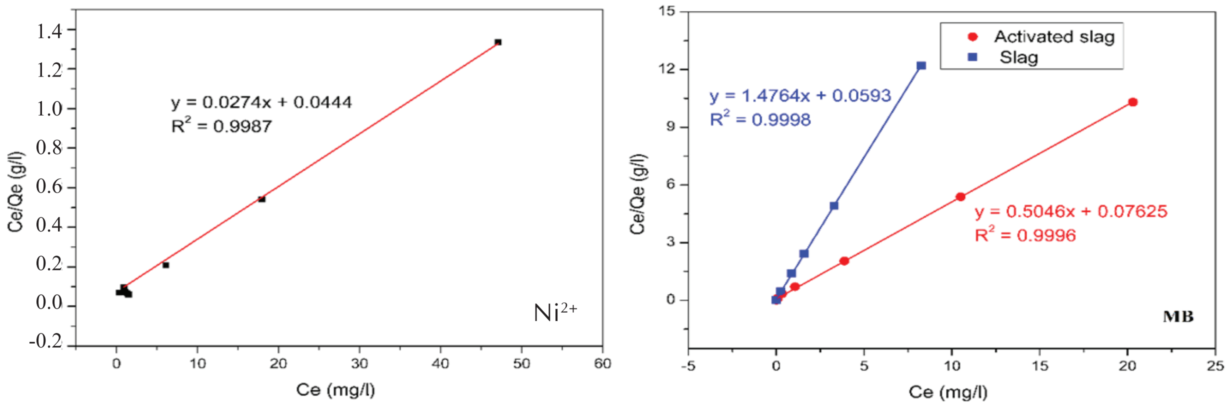

Fig. 7. Langmuir plots for Ni^{2+} and MB adsorption on slag samples.

It is shown that the effect of the initial concentration of Ni^{2+} and MB on their removal efficiency has a similar tendency. The percentage of removal was nearly 100% at a low concentration of Ni^{2+} (< 250 mg/l) and MB dye (< 6 mg/l). With the increase of the initial concentration of Ni^{2+} ions from 50 to 400 mg/l and of MB from 2 to 40 mg/l, the removal efficiency decreased from about 100 to 88.2, 34.5, and 50.02% for Ni^{2+}, MB (on the raw slag) and MB (on the activated slag), respectively. The adsorption capacity increased from about 4.8 to 35.3 mg/g for Ni^{2+} and from 0.2 to 1.97 mg/g for MB. At low initial concentrations, molecules of the adsorbates had more chance to react with the available active sites on the slag samples, resulting in an increase in the percentage removal. The decrease in the removal percentage at high concentrations of adsorbates can be explained that all the slag samples were limited by the adsorption sites; thus, the adsorption of Ni^{2+} and MB becomes restricted by the saturation of these adsorption sites [23].

Adsorption isotherms

The determination of the adsorption isotherm is important to indicate how adsorbent molecules were distributed between the liquid and the solid phase, and could be accurately used for design purposes and optimization of economical equipments. In this study, the Langmuir and Freundlich isotherm models were used to interpret equilibrium data of Ni^{2+} and MB(II) adsorption on the slag by utilizing the adsorption data obtained from the effect of initial concentrations. However, the experimental data were not correlated to the Freundlich model. Hence, only the results of the equilibrium data analysis using the Langmuir model are presented. The Langmuir isotherm considers the adsorbent surface as homogeneous with identical sites in terms of energy, and can be described by the following equation [24]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m \cdot K} + \frac{C_e}{Q_m} \quad (3)$$

where: C_e is the equilibrium concentration of Ni^{2+}/MB (mg/l), Q_e is the amount of Ni^{2+} or MB adsorbed at equilibrium (mg/g), Q_m is the maximum adsorption capacity of Ni^{2+}/MB (mg/g), and K is the Langmuir constant (l/mg). The value of Q_e was calculated using Equation 2. Q_m and K were calculated from a linear plot of C_e/Q_e against C_e with a slope and an intercept equal to $1/Q_m$ and $1/(Q_m.K)$, respectively. The constant separation factor R_L, whose value indicates the shape of the Langmuir isotherm, and predicts if an adsorption system is favourable or unfavourable, is calculated by the following equation [25]:

$$R_L = \frac{1}{1+K.C_o} \quad (4)$$

where: C_o is the initial concentration of adsorbate (mg/l), and K is the Langmuir adsorption constant (l/mg).

Figure 6 shows the adsorption isotherm of Ni^{2+} and MB dye on the slag samples. The Langmuir (C_e/Q_e vs. C_e) plots and the fitting parameters of the Langmuir isotherm for Ni^{2+} and MB adsorption are shown in Fig. 7 and Table 2, respectively.

As a result, the correlation coefficients obtained from the Langmuir equation for the adsorption of Ni^{2+} and MB dye on all slag samples were found to be from 0.9996 to 0.9998, indicating that the experimental data were well correlated with the Langmuir model. This means that the adsorption process was mainly monolayer on a homogeneous adsorbent surface. The Q_m values for Ni^{2+} and MB adsorption on the non-activated slag were 36.49 mg/g and 0.68 mg/g, respectively. While the maximum adsorption capacity of MB on the activated slag was 1.98 mg/g, about 2 times higher than that of the non-activated slag sample. The enhancement in the adsorption capacity of the acid-activated slag compared with the raw slag may be due to an increase in the number of active adsorption sites by acid treatment.

The value of the separation factor, R_L, indicates the adsorption nature of the adsorbate with the adsorbent. The adsorption process is unfavorable if $R_L > 1$, favorable if $0 < R_L < 1$, linear if $R_L = 1$, and irreversible if $R_L = 0$ [26]. In the present study, the values of R_L fall in between 0 and 1, and have confirmed that all slag samples are favorable for Ni^{2+} and MB adsorption under the experimental conditions.

Evaluation of adsorption thermodynamics

Table 2. Isotherm parameters for the adsorption of Ni^{2+} and MB onto slag.

Adsorbate-Adsorbent	Q_m (mg/l)	K (l/mg)	R^2	R_L
Ni^{2+} - slag	36.49	0.62	0.9987	0.0040
MB - slag	0.68	24.90	0.9998	0.0020
MB - act. slag	1.98	19.73	0.9996	0.0013

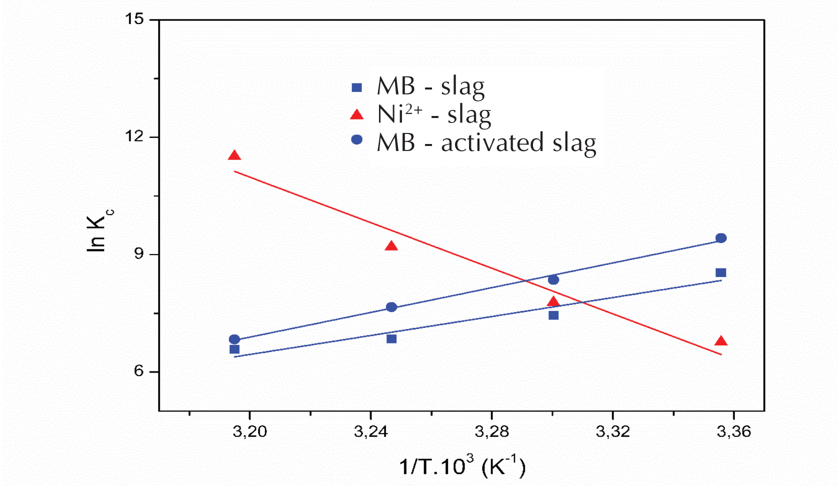

Fig. 8. Plot of lnKc as a function of reciprocal of temperature (1/T) for the adsorption of Ni^{2+} and MB by slag.

Table 3. Calculated thermodynamic parameters for Ni^{2+} and MB adsorption on slag.

Samples	ΔG° (kJ/mol)				ΔH° (kJ/mol)	ΔS° (J/mol/K)	R^2
	298K	*303K*	*308K*	*313K*			
Ni^{2+} - slag	-16.76	-19.59	-23.56	-29.96	242.10	866.12	0.940
MB - slag	-21.16	-18.76	-17.52	-17.12	-100.87	-269.12	0.897
MB - act. slag	-23.35	-21.05	-19.61	-17.78	-131.36	-362.99	0.991

To evaluate the thermodynamic parameters of Ni^{2+} and MB adsorption on the slag samples, the adsorption experiments were performed at different temperatures from 298 to 313 K. The equilibrium adsorption coefficient (K_c) for the adsorption process was calculated with the Equation 5 [27]:

$$K_c = \frac{C_{ad}}{C_e} \quad (5)$$

where: C_{ad} and C_e are equilibrium concentrations (mg/l) of Ni^{2+} and MB on the slag samples and in the solution, respectively. The thermodynamic parameters such as change in Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) are calculated using the following equations [28]:

$$\Delta G^o = - RTlnK_c \quad (6)$$

$$lnK_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (7)$$

where: R is the universal gas constant (8.314 J/mol/K), T is the absolute temperature (K). ΔH° and ΔS° were calculated from the slope -ΔH°/R and intercept ΔS°/R of the linear variation of ln K_c with the reciprocal of the temperature (1/T), as shown in Fig. 8. The obtained values of the thermodynamic parameters are presented in Table 3.

As can be observed from Table 3, the negative values of G° for nickel ions and MB adsorption at all temperatures indicate that the adsorption mechanism is a general spontaneous process and thermodynamically favorable [29]. The calculated thermodynamic parameters for MB adsorption on all the slag samples were negative. The negative values of ΔH° provide the exothermic nature of the adsorption process. The negative ΔSº indicates the decrease of the degree of freedom at the solid-liquid interface during the adsorption of MB on slag. For nickel adsorption, the standard enthalpy and the entropy values were obtained as 242.10 kJ/mol and 866.12 J/mol/K, respectively. The positive values of ΔHº and ΔSº reflect that the adsorption of Ni^{2+} by the slag is an endothermic process, and the randomness at the solid-liquid interface during the adsorption increases. This type of absorption can be explained in terms of the magnitude of ΔHº. Physisorption generally has low enthalpy values of 20-40 kJ/mol, while the enthapy of chemisorption lies in a range of 200-400 kJ/mol [30]. Therefore, nickel adsorption onto steel slag surface in the main can be attributed to a chemical adsorption process.

Conclusions

The steel slag was found to be a cheap material for the removal of Ni^{2+} and MB from aqueous solutions. The removal efficiency of Ni^{2+} and MB by the slag strongly depended on their initial concentration, contact time, initial pH, and adsorbent dose. The removal percentage of Ni^{2+} and MB dye was found to increase with an increase in the contact time, and the adsorbent dose was found to decrease with an increase in the initial adsorbate concentration. The optimal pH for Ni^{2+} removal was 5.0, which was lower than that for MB (pH 6.0). The adsorption of Ni^{2+} and MB dye on the steel slag saturated within 30 min and the adsorption processes could be well described by the Langmuir isotherm model, with maximum adsorption capacity of 36.49 mg/g for Ni^{2+} and 1.98 mg/g for MB. The activated slag had an adsorption capacity of about 2 times higher than the non-activated slag. The thermodynamic parameters indicate that the adsorption process is spontaneous in nature, thermodynamically favorable, endothermic (for Ni^{2+}), and exothermic (for MB). The results of this study show that the steel slag, a residue from steel plants that is readily available and easy to obtain at low cost, can be used as an effective adsorbent for the removal of Ni^{2+} ions and MB dye from wastewater.

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