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Single and binary adsorption of copper and nickel metal ions on nano zero valent iron (nZVI): a kinetic approach

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ABSTRACT

There is serious concern regarding copper and nickel, due to their persistent, non-biodegradable and toxic characteristics. This present study concerns the adsorption of copper (Cu(II)) and nickel (Ni(II)) ions onto nano zero valent iron (nZVI) from single and binary systems. Apart from low efficiency conventional adsorbents, nanoparticles such as nZVI and carbon nanotubes are promising adsorbents, as they have a higher adsorbent surface area and nano sized pores. Removal efficiencies are investigated for single and binary adsorption by considering the initial concentrations of copper and nickel. While the removal of copper was as high as 92% with the absence of nickel ion in aqueous solution, it decreased to 61% with 50 mg/L nickel ion concentration. Likewise, the 88% removal rate of nickel ion with the absence of copper, decreased to 70% with 50 mg/L copper ion concentration. Higher metal ion concentrations achieved even poorer results, by having 26% of removal efficiency, or less. It was also observed that the adsorption capacity of copper ion was higher than nickel ions in the binary system. For the highest total metal ion concentrations (300 mg/L), the adsorption capacity obtained was 960 mg/g in the binary system.

Keywords: Adsorption; Nano-zero valent iron (nZVI); Nickel removal; Copper removal

1. Introduction

Nickel and copper are materials mainly used in electronic industries and their bioaccumulation affects the ecological system. Nickel is mostly known for causing lung and nasal cancer. Because of their persistent characteristics, it is difficult to treat heavy metals by biological or chemical degradation.

In the literature, several methods, including adsorption [1–4], membrane filtration [6,7] and electroflocculation [8] have been applied to nickel and copper ions. Although many studies have been conducted for heavy metal treatment by activated carbon, there is a paucity of studies relating to their removal in lower concentrations [9,10]. Except from these low efficiency conventional adsorbents, by having higher adsorbent surface area and nano sized pores, nanoparticles such as nano zero valent iron (nZVI) and carbon nanotubes [11–14] are promising adsorbents.

Nanotechnology has attracted considerable attention in environmental engineering practices, due to properties such as high adsorption capacity and rapid responses. While the most applied application of nanotechnology in this field is soil remediation, water and wastewater treatment facilities have become popular. On heavy metal removal, studies show that nZVI is effectively used in heavy metal adsorption [12,13].

While adsorption of heavy metals by nanoparticles are widely studied in single systems, this present study concerns the adsorption of copper (Cu(II)) and nickel (Ni(II)) ions onto nano zero valent iron (nZVI) from single and binary systems with a kinetic approach. In the single adsorption system, the pH effect was investigated for both nickel and copper ions. Further studies were conducted by determining the optimum pH. While the effect of adsorbent concentration was investigated in the single adsorption system, the effect of initial metal ion concentration was investigated in the binary system.

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2. Materials and methods

2.1. Nanoparticle synthesis

In this study nZVI was synthesized using the borohydride method; the method most commonly used [15], as performed in the reaction given below:

$$Fe^{2+} + 2BH^{4-} + 6H_2O \rightarrow 2Fe^0 + 2B(OH)_3 + 7H_2\uparrow \quad (1)$$

$FeSO_4 \cdot 7H_2O$ solution was dissolved in a water:ethanol (30:70, v:v) mixture. In order to prevent aggregation, the method was enhanced with the addition of PEG. Borohydride solution was added dropwise at a rate of 30 mL/min to iron sulfate solution. After obtaining nanoparticles, the mixture was washed with ethanol and pure water in order to inhibit the negative effects of SO_4^{2-} and Br^- ions. The nZVI particle size was measured at 68.7 nm using a zetasizer. TEM images of the produced nZVI also showed that nZVI has a spherical and chain structure.

2.2. Experimental studies

All the experiments were examined with synthetic samples prepared by $CuSO_4$ and $NiCl_2 \cdot 6H_2O$ (MERCK). In the single adsorption system, the experimental sets were conducted in 100 mL total sample volume with different concentrations of nZVI concentration. In the binary system, the experimental sets were contained in optimum pH and the concentration of nZVI was shaken at 150 rpm and kept at a constant temperature of 20ºC for 30 min. The resulting samples were centrifuged at 6000 rpm for 5 min for the separation of nanoparticles. The initial and effluent copper and nickel analysis was applied using a Perkin Elmer Atomic Adsorption Spectrometer C-400. For the binary system, in order to observe interactions between copper and nickel ion, it was studied using five different concentrations of both metals.

3. Results and discussion

3.1. Single adsorption of Nickel and Copper

3.1.1. Effect of Initial pH

The experimental setup was conducted to state the pH effect on the removal of copper and nickel in single adsorption, in which the pH was adjusted from pH 2 to 12. The concentration of synthetic samples was 100 mg/L and the applied adsorbent concentration was 100 mg/L for 30 min of reaction time.

In Fig. 2a, it can be observed that there is a sharp increase in the removal of copper and nickel ions at around pH 4 and pH 5, respectively. In a study by Dawodu et al. [17] it is explained that it is the pH value that makes the surface of the adsorbent negative, and favorable for the

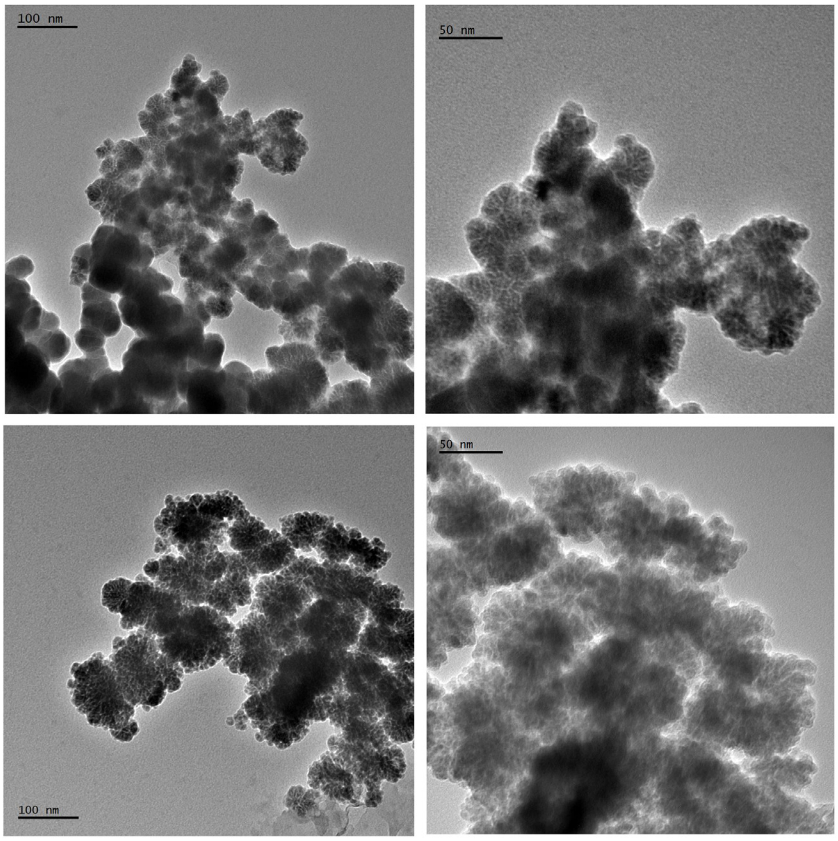

Fig. 1. TEM image of nZVI.

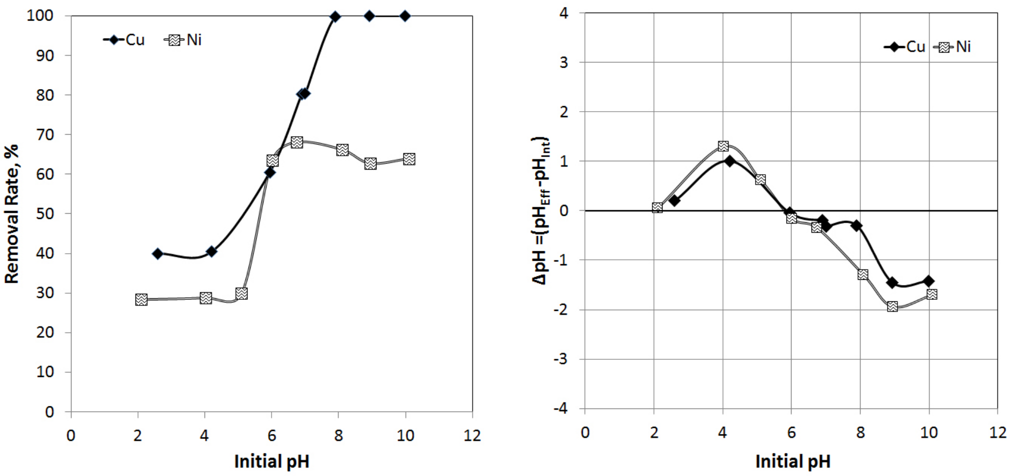

Fig. 2. (Right) Effect of initial pH on copper and nickel removal (Left) pH variance in different initial pH.

adsorption of positively charged ions. The removal rates for nickel in pH 6 and 7 were 63% and 68%, respectively. There was no significant change in the removal rates with a pH higher than pH 7. Similarly, it can also be seen in Fig. 2 (Right) that the removal rates were considerably lower with a pH adjusted to less than pH 6. However, in copper removal, the removal rates obtained were 80%, 80% and 99% for pH 6, 7 and 8, respectively. In the experiments with a pH higher than pH 8, the removal rate was almost 100%. This can be explained by the hydroxyl reaction and hydroxyl settlement with copper with high pH. According to pH-Eh diagrams [18], copper is in a solid form of $Cu(OH)_2$ with pH 8 and higher, and nickel is in an aqueous form, even in pH 10. Several authors who investigated metal adsorption by different adsorbents also observed a similar trend: i.e. removal by chitosan immobilized bentonite [19], kaolinite clay [17], iron oxide-coated sand [20] and γ-alumina nanoparticles [21]. In light of the data that was obtained, a further study was conducted with pH 6.75 and pH 6.9 for nickel and copper samples, which is the original pH for each sample.

Effluent pH and the difference between the initial and effluent pH was also observed, as shown in Fig. 2 (Left). While there were no significant changes in effluent pH with the studies applied in pH 6 and pH 7, in the studies with pH values lower and higher than pH 6 and 7 there were substantial changes, especially by increasing to pH 7 from a lower initial pH and vice versa. In initial pH concentrations higher than pH 7, a decrease in effluent pH can be caused by the rapid reaction of metal ions with hydroxide through the formation of metal hydroxides [16]. Correspondingly, the high concentration of H^+ in lower initial pH can cause corrosion of nZVI by consuming water to generate OH^-; therefore, the effluent pH in low initial pH is increased

3.1.2. Effect of adsorbent concentration

By arranging initial concentrations of Ni and Cu in 100 mg/L for each sample, the effect of adsorbent concentration was investigated. Experiments were conducted in 100 mL of sample volume in 150 rpm for 30 min. Selected concentrations for nZVI were 50, 100, 200 and 400 mg/L. The obtained removal rates and calculated adsorption capacities can be seen in Fig. 3.

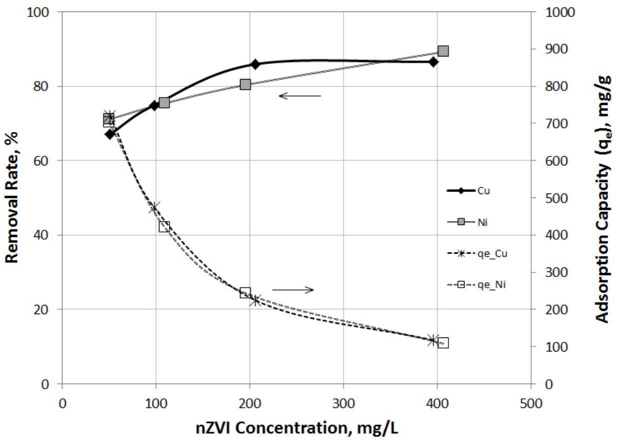

Fig. 3. Removal rates and adsorption capacities of Cu(II) and Ni(II) in nZVI concentration variations.

It can be gathered from Fig. 3 that, removal rates for each samples were increased with adsorbent concentration as expected. A slight increase was obtained between 200 and 400 mg/L adsorbent concentration for copper samples. This gives the information about the optimum adsorbent concentration for copper removal.

While it was observed that there was a linear increase at a slight rate with increased adsorbent concentration for nickel removal, the 200 mg/L nZVI concentration was selected for both nickel and copper removal for comparison with the data in the binary adsorption experiments.

Adsorption capacities can also be seen in Fig. 3. With nZVI, both ions gave similar responses, while adsorption capacities for the 200 mg/L nZVI concentration were 236 and 230 mg/g for 100 mg/L concentrations for nickel and copper, respectively.

3.2. Binary adsorption of Nickel and Copper

In light of the data obtained in the single adsorption system, the binary system was accompanied with different copper and nickel concentrations and their effect on each other. A matrix was prepared with 10, 25, 50, 100 and 150 mg/L concentrations of copper and nickel ions, to detect the effect of copper ion concentration on nickel ion removal, and vice versa. Single metal adsorption was also studied for both metal ions, in order to compare data in the binary system.

In Fig. 4, the effect of copper concentration on nickel removal can be seen. A higher decrease in the removal rate is observed in the binary system (removal of copper and nickel ion in same sample) than with the single metal adsorption system. In the studies with 10, 25 and 50 mg/L nickel concentration without copper ion, the removal rates were 88, 85 and 81%, respectively; while when the lowest studied concentration of copper concentration (approximately 10 mg/L) was applied, removal rates decreased to 81, 78 and 70% for 10, 25 and 50 mg/L initial copper concentration, respectively. These decreases were similar as in the literature [17,19–21]. In the studies with higher initial concentration of copper than 25 mg/L, a high decrease in nickel removal was observed. The lowest removal rate of nickel was obtained with the sample containing 150 mg/L copper and 150 mg/L nickel ions, at 20% (C_{e-Ni}/C_{o-Ni}:0,80). In addition, it was also be noted that a removal rate higher than 70% was observed for 150 mg/L copper concentrations, in single adsorption. Comparable to nickel removal, the effect of nickel concentration in copper removal is given in Fig. 5. The removal rates of copper with 10, 25 and 50 mg/L in the single adsorption system was approximately 92%. With the addition of nickel ion in concentrations of 10 mg/L, removal rates decreased to 86, 76 and 61%, respectively. The decrease in nickel removal was lower than copper removal. With initial nickel concentrations higher than 25 mg/L for all copper concentrations, the decrease in removal was considerably lower when compared to nickel removal. The removal rate of copper was lowest, at 26% with a 150 mg/L initial concentration of both nickel and copper. Moreover, it should be noted that, for single nickel adsorption, the removal rate was higher than 70% with initial nickel concentrations of 150 mg/L.

Fig. 6 is presenting nickel and copper ion adsorption capacities versus effulent nickel and copper ion concentrations. Total heavy metal adsorption capacities were calculated by considering total adsorped heavy metal ions in total metal ion concentration. Nickel and copper adsoption capacites were increased with the increase in total metal ion concentration, and copper adsorption capacities are higher than nickel adsorption, as given in researches by different adsorbants [17,19–21]. For the highest total metal concentration of 300 mg/L (150 mg/L nickel and 150 mg/L copper ion concentration) adsorption capacity was 960 mg/g .

3.3. Adsorption isoterm models in single and binary adsorption systems

In order to describe the adsorption process, adsorption isotherms were applied. The relationship of the pollutant amount adsorbed by the unit adsorbent amount, at a constant temperature with the equilibrium solution concentration (or pressure), is termed the adsorption isotherm. It is a function of the substance amount, temperature, concentration, pressure, or equilibrium pressure adsorbed by the unit mass of the adsorbent when the system is at equilibrium during the adsorption. Freundlich and Langmuir developed the equations commonly used to assess experimental isotherm data. The Langmuir isotherm is expressed in Eq. (2) as follows:

$$q_e = \frac{q_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \tag{2}$$

where q_e: unit mass substance adsorbed by unit mass adsorbent (mg/g), C_e: Nickel concentration remaining in the solution after adsorption, q_{max}: maximum adsorption capacity (mg/g), and K_L empirical coefficients. The Freundlich isotherm is expressed in Eq. (3) as follows:

$$q_e = K_f C_e^{1/n} \tag{3}$$

where q_e: unit mass substance adsorbed by unit mass adsorbent (mg/g), K_f: Freundlich capacity factor (mg/g), C_e: Effluent nickel concentration, $1/n$: Freundlich density parameter.

In order to compare isotherm data, all experiments were conducted using 200 mg/L nZVI concentration. When Langmuir and Freundlich isotherm models are evaluated with experimental data for both the single and binary system, the Langmuir isotherm is found to be more satisfactory for both single and binary system with high correlation coefficients (>0,99) (Table 1). In the binary system for copper

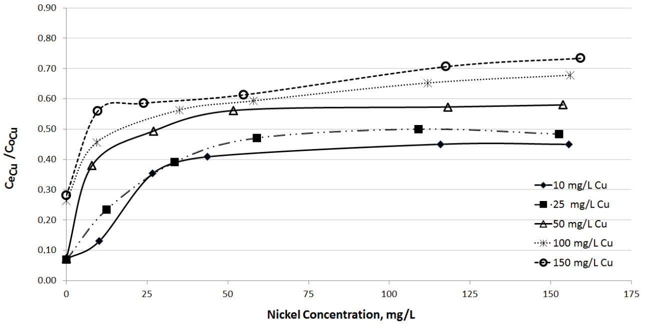

Fig. 4. Nickel removal indifferent initial nickel concentrations.

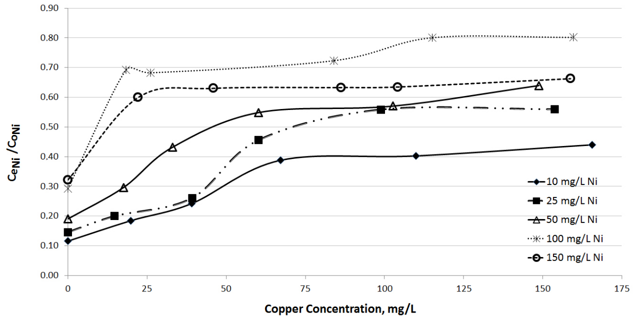

Fig. 5. Copper removal indifferent initial copper concentrations.

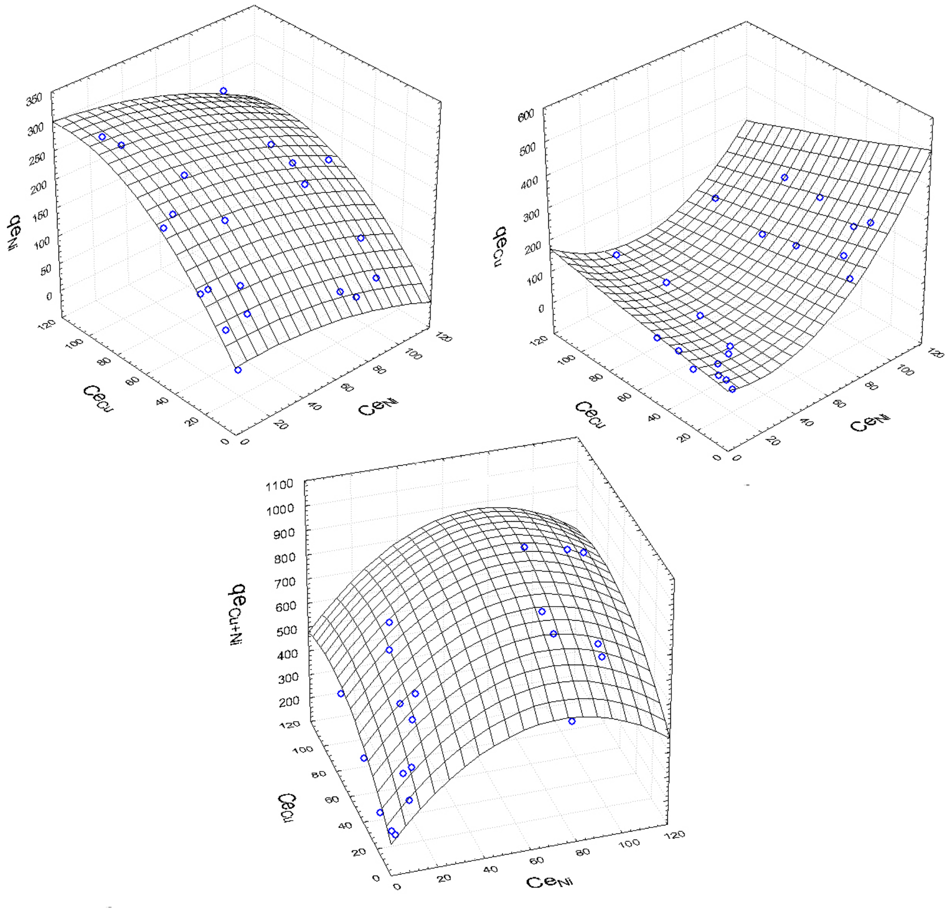

Fig. 6. Nickel (upper left), copper (upper right) and total heavy metal adsorption capacities indifferent nickel and copper effluents in binary system.

Table 1
Langmuir and Freundlich regression coefficients for single and binary system

	Single adsorption system		Binary adsorption system	
Isotherm	Nickel	Copper	Nickel	Copper
Langmuir	0.993	0.997	0.996	0.998
Freundlich	0.976	0.931	0.964	0.985

Table 2
Langmuir isotherm coefficients

	Single adsorption system		Binary adsorption system	
Coefficient	Nickel	Copper	Nickel	Copper
q_{max}	666.67	625	334.55	474.85
K_L	0.052	0.127	0.038	0.016
R^2	0.993	0.997	0.996	0.998

ion, the nickel concentration was 100 mg/L and, vice versa. The Langmuir isotherm coefficients obtained are given in Table 2. Maximum adsorption capacities are almost comparable at 666.67 mg/g and 625 mg/g for nickel and copper in the single adsorption system with 200 mg/L nZVI, respectively. For the binary system, adsorption capacities are 334.55 mg/g and 474.85mg/g for nickel and copper ion, which is an indication that copper adsorption is more favorable than nickel adsorption.

Comparisons of the experimental and calculated adsorption capacities for copper and nickel ions, according to the Langmuir isotherm model, are presented in Fig. 7 for both the single and binary adsorption systems. Nickel ion adsorption capacities were calculated by considering the initial nickel ion concentration, and similarly the copper ion concentration was used for the copper ion adsorption capacities. Fig. 7 indicates that all Langmuir isotherm models could represent the experimental adsorption data for both the single and binary systems. Even if the initial metal ion concentration was the same for both the single and binary adsorption systems, the effluent metal concentration C_e is lower and the adsorption capacities are higher in the single adsorption rather than the binary adsorption, as expected. For both systems, the copper adsorption capacities were higher than the nickel.

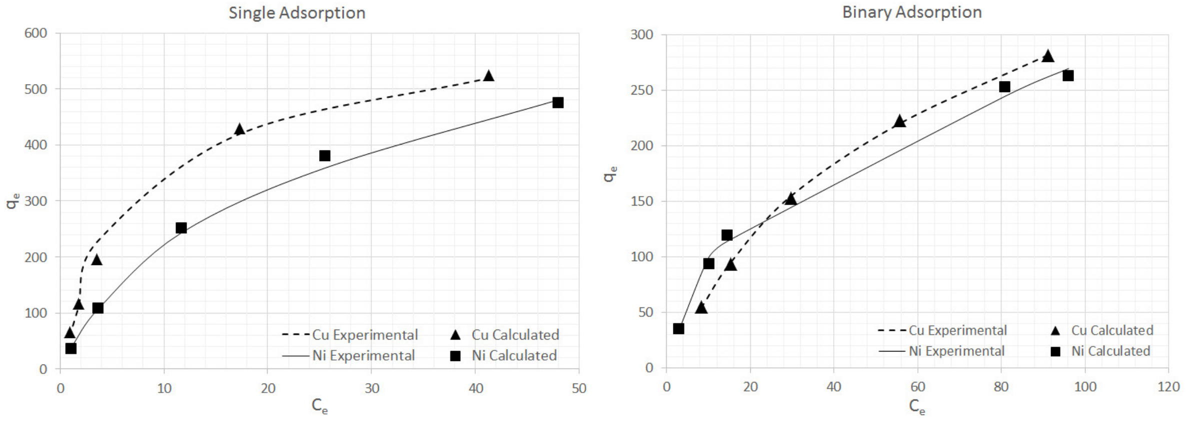

Fig. 7. Langmuir isotherm modeling for single and binary adsorption system.

4. Conclusion

For a single adsorption system, an adsorbent concentration of 100 mg/L nZVI is sufficient for 100 mg/L metal ion concentrations, and also has a higher adsorption capacity (approximately 500 mg/g) than conventional adsorbents, such as activated carbon. Synthesized nZVI is a promising adsorbent, even in high concentrations of nickel and copper metal ions, as 150 mg/L with 70% and has a higher removal rate in single adsorption. When binary metal adsorption was compared with single metal adsorption, the removal rates were notably decreased, as expected. Removal rates were higher than 75% when both initial metal concentrations were lower than 25 mg/L. For highest total metal ion concentrations (300 mg/L) the adsorption capacity obtained was 960 mg/g in the binary system. Based on the obtained data, nickel removal was lower than copper removal both in single and binary adsorption systems. Moreover, the Langmuir isotherm model showed the best fit for single and binary adsorption systems.

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