Adsorption of Copper Metal Ion from Aqueous Solution by Nanoscale Zero Valent Iron (nZVI) Supported on Activated Carbon

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Abstract

Copper is from one of the most important heavy metals, which adheres to the ecological system by harmful human activities. It is toxic, persistent, and non-biodegradable metal, which causes environmental pollution in both the atmosphere and aquatic environment. Copper pollution found in undesirable concentrations in industrial wastewaters especially from electronics industries, cooling systems and plating industry. Physical methods are mostly applied to remove Cu(II) including adsorption and membrane processes. Nanoparticles (e.g. nano zero valent iron (nZVI), carbon nanotubes, titanium dioxide nanoparticle) have been considered to be promising alternatives to conventional adsorbents. They have advantages by having more surface area and nano-sized pores, which helps to adsorb more molecules. In this study, in order to enhance adsorption by activated carbon and lower the cost of nanoparticle synthesis, nZVI is synthesized on activated carbon(AC-nZVI). It was investigated for its effectiveness in copper removal from aqueous solution. The effect of AC-nZVI dosage, pH and the initial concentration of Cu were investigated. Adsorption capacities are obtained for nZVI and AC-nZVI as 414 mg/g and 510 mg/g, respectively. 200mg/L AC-nZVI concentration was determined as sufficient for %96 removal rate. Langmuir isotherm gave the best fit and the maximum adsorption capacity according to Langmuir isotherm is calculated as 588,24 mg/g.

Key words:Adsorption, Nano-Zero Valent Iron (nZVI), Activated Carbon, Copper Removal

1. Introduction

Nanotechnology became a popular topic in environmental engineering practices with increasing number of studies on soil remediation and also water and wastewater pollution applications. Conducted studies on nano zero valent iron, especially on heavy metal removal, demonstrated that it is effective by means of its high adsorption capacity [1-4].

Copper is a material used in the electronics industries, cooling systems by having the characteristic feature of high electrical and thermal conductivity. Also it is used as plating material due to its rustproof specification. Heavy metals enter to the ecological system by human activities and bioaccumulate through food chains and lead carcinogenic effects on human[4-6]. They have persistent and non-biodegradable characteristics, which cause environmental pollution in both atmospheric and aquatic environment [4-7]. Several techniques have been applied for heavy metal removal including adsorption by activated carbon, natural low-cost adsorbents and gamma alumina, ion-exchange system, membrane processes, electrochemical applications [5-6,8-12]. Many studies have demonstrated that nano zero valent iron (nZVI) can effectively be used to remove chrome and arsenic as heavy metals [13-16].

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The purpose of this study is to enhance adsorption by supporting nano zero valent iron on activated carbon. For this aim, nZVIis synthesized on activated carbon and it is investigated for its effectiveness in copper removal. The effect of AC-nZVI dosage, reaction time and initial copper concentration is also investigated.

2. Materials and Method

2.1. Synthesis of AC-nZVI

In order to clean powdered activated carbon before synthesis of nZVI-coated activated carbon (AC-nZVI), powder activated carbon was kept in 5% nitric acid solution for 1 day. Then, it was washed with ultra-pure water and ethanol to remove acid and ethanol content was lost by keeping in oven over night. AC-nZVIwas synthesized in 50% ratio with nZVI. For this, the predicted amount of nZVI is calculated with reaction occurred in borohydride method.

$$Fe^{2+} + 2BH_4^- + 6H_2O \rightarrow 2Fe^0 + 2B(OH)_3 + 7H_2\uparrow$$
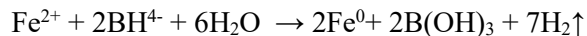
$FeSO_4.7H_2O$ solution was dissolved in water:ethanol (30:70, v:v) mixture. AC was added in the same predicted amount of synthesized nZVI into this solution. To prevent aggregation PEG 2000 was also used. $NaBH_4$ was added dropwise with the rate of 20 mL/min to iron sulfate solution to occur above reaction. The obtained mixture is containing nZVI coated activated carbon particles and it was washed with ethanol and pure water to inhibit sulfate and boron ions' negative effects. In order to demonstrate activated carbon effect, nZVI is synthesized by the same method.

2.2. Experimental Method

$CuSO_4$ (MERCK) was used to prepare the synthetic samples. The experiment sets were conducted with 100 mL of copper containing synthetic samples with different amount of AC-nZVI particles and shaked at 150 rpm and 20ºC constant temperature. Prepared samples were centrifuged at 6000 rpm for 5 minutes for separation of AC-nZVI particles. The initial and effluent copper analysis was executed in Perkin Elmer Atomic AdsorptionSpectrometer C-400.

2.3. Isotherms

Adsorption isotherms are the most common calculations to describe adsorption process. Isotherms give the relationship between pollutant concentration adsorbed on known amount of adsorbent and equilibrium solution concentration. The equations, commonly used to assess the experimental isotherm data, were developed by Freundlich and Langmuir.

The Freundlich isotherm is expressed as follows [17]:

$$q_e = K_f C_e^{1/n}$$

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

The Langmuir isotherm, in turn, is expressed as follows[17]:

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

where, q_e: unit mass substance adsorbed by unit mass adsorbent (mg/g), C_e: effluent pollutant concentration (mg/L), q_{max}: maximum adsorption capacity (mg/g), and K_L empirical coefficients.

3. Results and Discussion

3.1. Effect of Initial Copper Concentration on Removal

In order to demonstrate the effect of copper concentration on removal rate, the research was established in 100 ml of sample volume with 10, 25, 50, 100 and 150 mg/L copper ion concentration and 400 mg/L concentration of AC-nZVI as adsorbent. The samples were shaked for 30 minutes in 150 rpm at 20ºC of stable temperature. After determined contact time, the samples were centrifuged at 6000 rpm for 5 minutes to remove particles from water. In Figure 1, removal rates and adsorption capacity is stated in terms of obtained data.
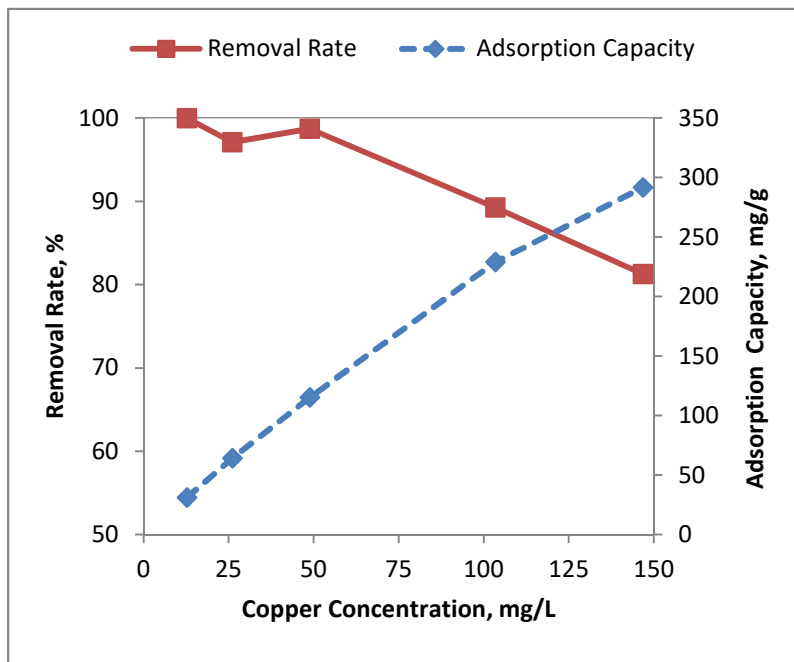

Figure 1. Effect of Initial Copper Concentration

It can be seen in Figure 1 that removal rate was decreased after 50 mg/L concentration of copper ion. The removal rate with 10, 25 and 50 mg/L initial concentration was obtained in higher rate of 98%. In addition to this removal rate was still higher than 80% in the highest selected copper concentration of 150 mg/L. Adsorption capacity was increased with the increment of initial copper concentration as expected. The slope of adsorption capacity plot was almost linear. It can be concluded that the maximum adsorption capacity is not achieved with 150 mg/L copper ion

concentration.

3.2. Effect of Contact Time and AC-nZVI Concentration on Removal

Experiments were conducted to determine the effect of contact time and AC-nZVI concentration on removal rate by using 2-120 minutes contact time and 50-400 mg/L AC-nZVI concentration at 150 rpm at 20ºC. The concentration of copper was selected as 50 mg/L. Different samples was taken in 2, 5, 10, 20, 30, 60 and 120 minutes and centrifuged immediately at 6000 rpm for 5 minutes to remove AC-nZVI particles from water for copper analysis. Figure 2 and Figure 3 are demonstrating the effect of contact time and adsorbent concentration.

It is shown in Figure 2 that the large portion of removal was captured in the first 5 minutes and removal was almost stable for each experiments after 10 minutes of contact time. This can be due to reach of maximum adsorption capacity. It is also observed that the removal efficiency increased with the increase of adsorbent concentration as expected. After 200 mg/L of adsorbent concentration the increase trend was reduced. The highest removal rate of 99.50% was achieved with 400 mg/L after 20 minutes of contact time. 200 mg/L AC-nZVI concentration can be selected as optimum concentration in according with low increase in higher adsorbent concentration.
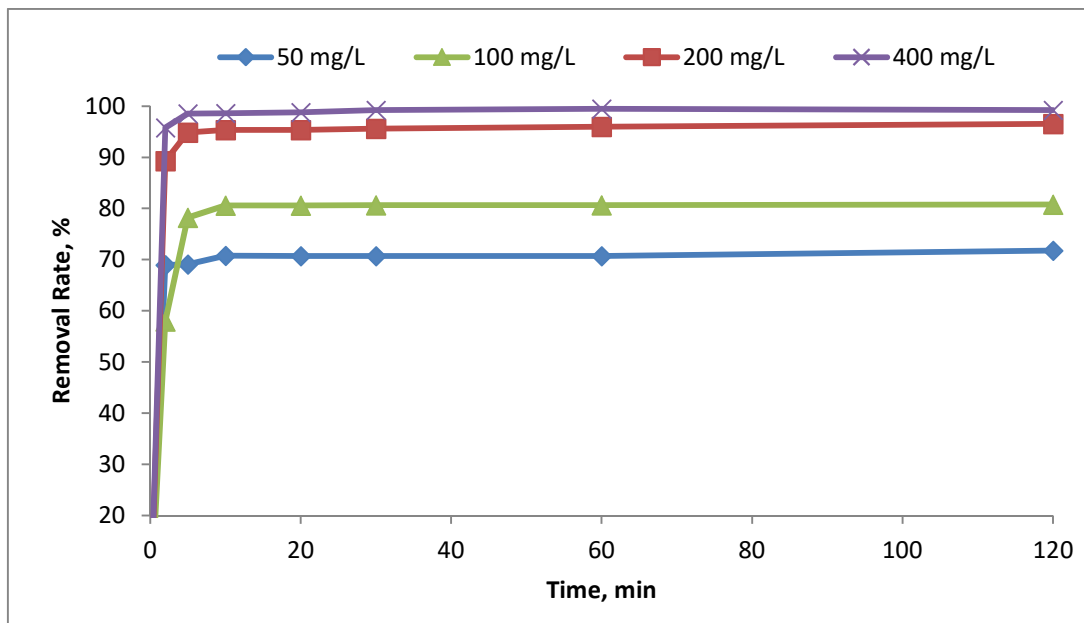

Figure 2. Effect of Contact Time and Adsorbent Concentration on Removal Rate

In Figure 3 the adsorption capacity variance according to adsorbent concentration is shown. As the adsorption capacity was 790 mg/g for 50 mg/L adsorbent concentration, it is decreased with adsorbent concentration as expected. Activated carbon was supported with nZVI in order to enhance removal rate.
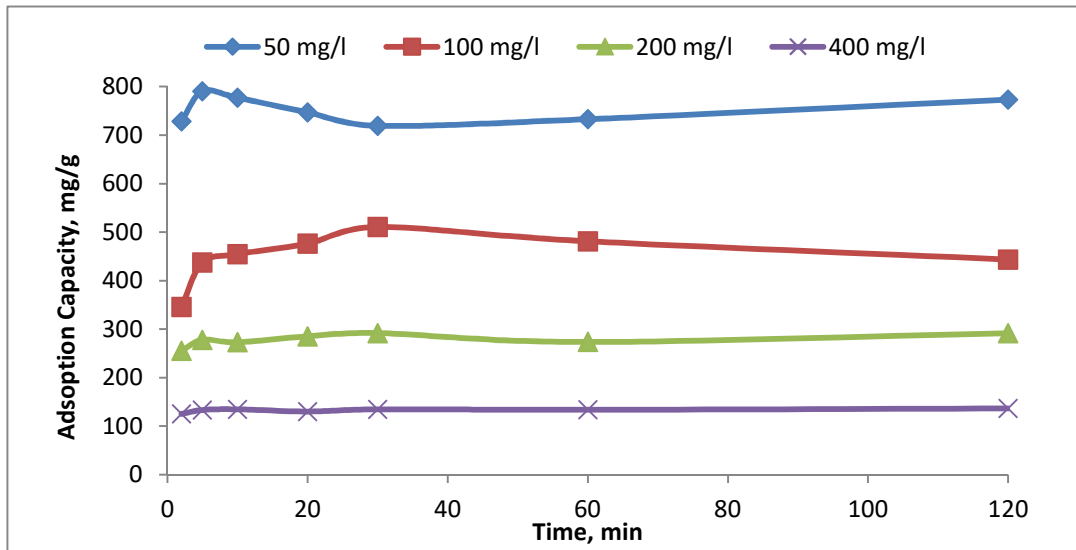
Figure 3. Change in Adsorption Capacity by Contact Time and Adsorbent Concentration

As the maximum adsorption capacity of activated carbon was changing between 6 – 39 mg/g for copper ion removal [18-20], the maximum adsorption capacity of AC-nZVI was obtained at 790 mg/g. In Figure 4, adsorption capacity in the effect of adsorbent concentration can be seen for nZVI and AC-nZVI. The experiments were conducted for 30 minutes at same adsorbent concentration and 50 mg/L copper ion concentration. While adsorption capacity of nZVI for 100 mg/L adsorbent concentration is 414 mg/g, it was 510 mg/g for AC-nZVI. Adsorption capacity is increase by supporting activated carbon with nZVI.
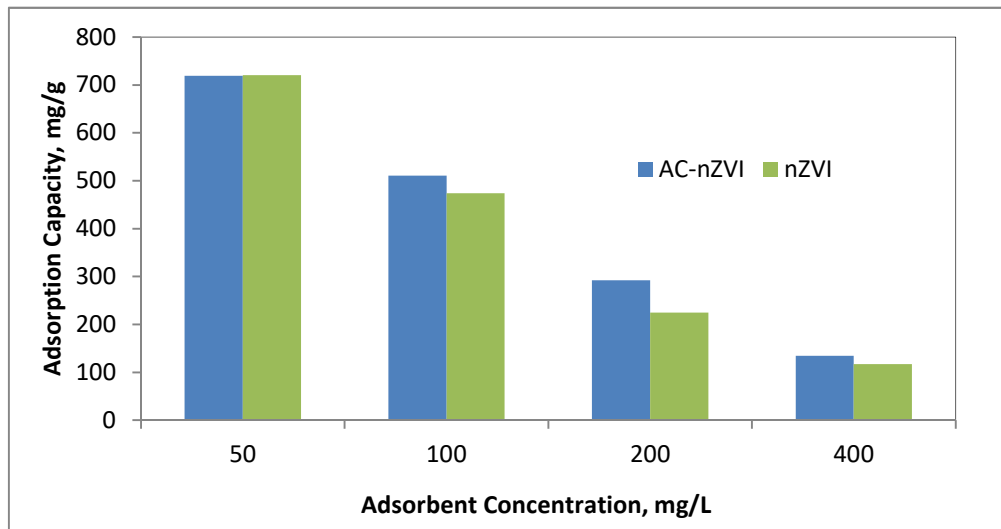

Figure 4. Difference of Adsorption Capacities of nZVI and AC-nZVI

3.3. Adsorption Isotherm

R^2 (Determination Coefficient) is a positive value between 0 and 1; and the closer the value 1 shows that the distribution is consistent. Isotherm plots belong to Freundlich and Langmuir

Isotherm can be seen in Figure 5 and the calculated coefficient is given in Table 1. By considering determination coefficients of isotherm plots, Langmuir isotherm shows the most suitable isotherm. According to Langmuir isotherm, maximum adsorption capacity is calculated as 588,24 mg/g.
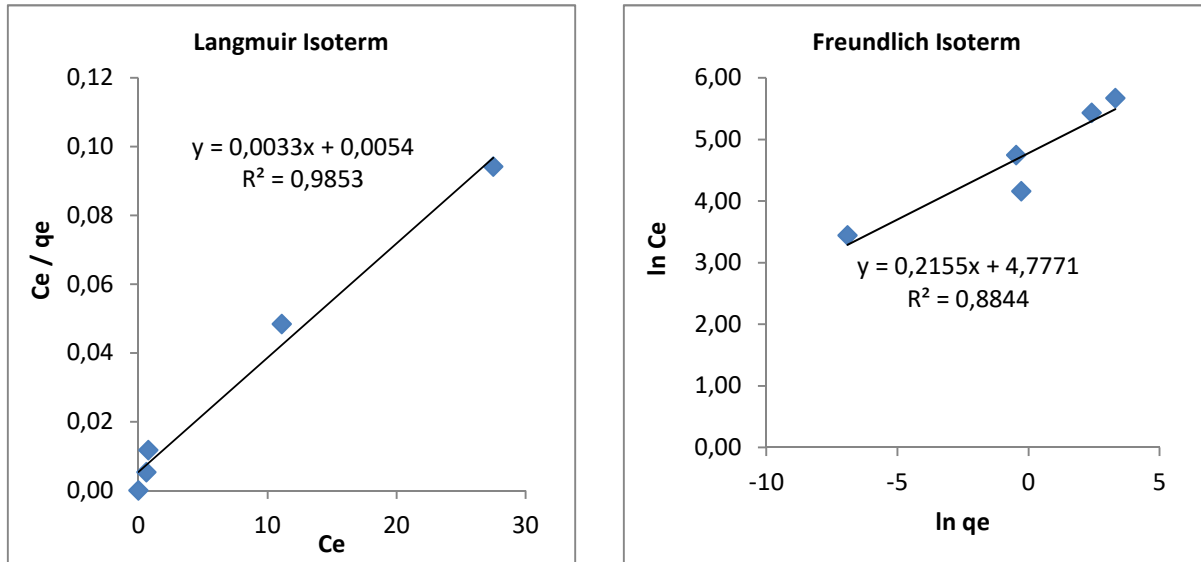

Figure 5. Langmuir and Freundlich Isotherm Plots

Table 1. Coefficient of Isotherms

Langmuir Isotherm		Freundlich Isotherm	
q_{max}	588,24	K_f	237,508
K_L	0,630	n	4,640
R^2	0,985	R^2	0,884

Conclusions

In this study, it is aimed to enhance nZVI adsorption capacity by supporting activated carbon in copper ion removal. Effect of initial copper concentration, contact time and adsorbent concentration was investigated and thereafter the adsorption capacity variance of activated carbon, nZVI and AC-nZVI was disclosed. Even the initial concentration of copper was as high as 150 mg/L, removal rate was obtained at 81% with 400 mg/L AC-nZVI concentration in 30 minutes contact time. 50 mg/L of the selected lowest initial copper concentration was almost totally removed by AC-nZVI. The large portion of removal was achieved at 5 minutes of contact time. The removal rate was increased with the concentration of AC-nZVI, however the difference

on removal rate belong to 200 mg/L and 400mg/L AC-nZVI concentration was negligible. 200mg/L AC-nZVI concentration was determined to be sufficient for %96 removal rate. While the copper ion adsorption capacity of activated carbon was 6-39 mg/g according to literature, the adsorption capacities belong to nZVI and AC-nZVI is 414 mg/g and 510 mg/g, respectively. This shows the effect of nZVI supported on activated carbon to remove copper from the solution. Adsorption capacity of activated carbon is increased by supporting nZVI on activated carbon. This gives an advantage of lower adsorbent concentration and higher removal rate in the removal of copper metal ions. Langmuir isotherm give the best fit and the maximum adsorption capacity according to Langmuir isotherm is calculated as 588,24 mg/g.

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