Optimizing Cu(II) removal from aqueous solution by magnetic nanoparticles immobilized on activated carbon using Taguchi method

Mohammad Javad Ebrahimi Zarandi, Mahmoud Reza Sohrabi, Morteza Khosravi, Nafiseh Mansouriieh, Mehran Davallo and Azita Khosravan

ABSTRACT

This study synthesized magnetic nanoparticles (Fe₃O₄) immobilized on activated carbon (AC) and used them as an effective adsorbent for Cu(II) removal from aqueous solution. The effect of three parameters, including the concentration of Cu(II), dosage of Fe₃O₄/AC magnetic nanocomposite and pH on the removal of Cu(II) using Fe₃O₄/AC nanocomposite were studied. In order to examine and describe the optimum condition for each of the mentioned parameters, Taguchi’s optimization method was used in a batch system and L₉ orthogonal array was used for the experimental design. The removal percentage (R%) of Cu(II) and uptake capacity (q) were transformed into an accurate signal-to-noise ratio (S/N) for a ‘larger-the-better’ response. Taguchi results, which were analyzed based on choosing the best run by examining the S/N, were statistically tested using analysis of variance; the tests showed that all the parameters’ main effects were significant within a 95% confidence level. The best conditions for removal of Cu(II) were determined at pH of 7, nanocomposite dosage of 0.1 gL⁻¹/C₀, and initial Cu(II) concentration of 20 mg L⁻¹/C₀ at constant temperature of 25°C. Generally, the results showed that the simple Taguchi’s method is suitable to optimize the Cu(II) removal experiments.

Key words | activated carbon, copper ion, magnetic nanoparticles, orthogonal Taguchi optimization

INTRODUCTION

Water contamination with toxic heavy-metal ions tends to be of great concern when it comes to the health of humans as well as other forms of life. Although the emissions of hazardous metallic substances to the aquatic environment can occur at every stage of their life cycle, from production to disposal, and discharge of untreated industrial effluents could be considered as a major cause of hazard (Komárek et al. 2010). Typically, copper ions from untreated effluents of mining operations, chemical manufacturing, and electronic and pharmaceutical industries can contaminate the food chain and have lethal effects on vital organs of humans (Murphy & Hathaway 2003; Hites & Raff 2012). Consequently, exploring effective methods to remove these heavy metal ions from water on various industrial effluents is required.

Currently, several approaches are being used to remove heavy metal ions from aqueous effluents, including ion exchange (Dabrowski et al. 2004), chelation (Mozaffari et al. 2007), chemical precipitation (Fu & Wang 2011), electrochemical treatment (Hunsom et al. 2005), reverse osmosis (Ozaki et al. 2000), membrane (Bolzonella et al. 2010), and biosorption (Mudhoo et al. 2012). However, the application of these methods have been hindered as a result of some inherent limitations, involving high capital and maintenance cost, expensive equipment, high sensitivity to operational conditions, significant energy consumption, incomplete metal removal or sludge generation (Babel & Kurniawan 2003). Generally, adsorption has indeed been considered as the most popular and widely used process for heavy metal applications removal due to its high efficiency, cost effectiveness and easy handling (Lim & Aris 2014). As such, diverse ranges of commercially available adsorbents, such as activated carbons (AC) and polymers...
as well as low-cost adsorbents from agricultural and food wastes, soil and industrial by-products were evaluated (Mishra & Patel 2009; Dragan et al. 2010; Lim & Aris 2014).

AC have attracted significant attention for diversified applications in pollutant removal (Gupta et al. 2011), remediation (Mohan & Pittman 2006) and catalyst supports due to the high specific surface area, high porosity, and adsorption capacity as well as excellent thermal and chemical stabilities and low acid/base reactivity (He et al. 2015). As a result, AC is of interest to many affected areas in economic sectors and industries as well as different pharmaceutical, food, petroleum, chemical sectors, and particularly for the treatment of drinking water, and industrial and urban wastewater (Yang et al. 2011; Hadi et al. 2015). As an effective adsorbent, AC is largely used to remove pollutants from liquid or gaseous phases and to purify or recover valuable chemicals (Ahn et al. 2009; Marta Sevilla & Fuertes 2012). In spite of its interesting properties and different applications, AC needs to be modified for specific application (Bhatnagar et al. 2013). Among all modifying methods of acid, base, ozone, plasma, and microwave treatments, impregnation with metals and metal oxides and their nanoparticles especially is gaining wide interest due to the expressively increased adsorption capacity (Tchomgui-Kamga et al. 2010; Vaughan & Reed 2005; Sharma & Srivastava 2011; Vitela-Rodriguez & Rangel-Mendez 2013). However, these materials are difficult to re-collect from water and cannot be used to treat the wide range of metal-laden wastewater effectively (Peng et al. 2012). Magnetic nanoparticles in addition to the higher surface area than the bulk materials, offer an easy recovery by an external magnetic field (Sharma & Srivastava 2011; Simeonidis et al. 2015; Kalantari et al. 2015, 2014). Among these, materials such as (Fe3O4) nanoparticles, could easily be synthesized and widely used as a potential adsorbent for removing lots of contaminants (Zhang et al. 2013).

In order to optimize the effect of the variables on the performance of the systems and minimize the overall testing time and the experimental costs, different multivariate modeling methods have been reported so far (Zolgharnein et al. 2013; Dorraj et al. 2015; Mansouriieh et al. 2015; Yan & Lin 2015).

Multivariate optimization leads to more information on variables, their interactions and impact on the performance after running fewer experiments than that of the conventional one-at-a-time method (Landaburu-Aguirre et al. 2010; Abdollahi et al. 2015). Among various multivariate optimization approaches, the Taguchi method provides an efficient and systematic approach to optimize designs for quality, performance and cost, particularly when variables are many (Vlachogiannis & Vlachonis 2003; Mousavi et al. 2007; Wang & Huang 2007). The crossed array layout of the method consists of an inner and an outer array where the inner array is made up of the orthogonal array (OA) selected from all possible combinations of the controllable factors and the optimum experimental conditions can be determined easily using this array (Elizalde-González & Diaz 2010).

Recently, chemical and environmental engineers have started applying Taguchi’s design of experimental methodology in various studies. Copper removal by adsorption on amine modified silica optimized using experimental condition based on Taguchi design (Da’na & Sayari 2011); Cu(II) separation by electrodiagnosis (Mohammadi et al. 2004) and adsorption of metal ions onto rice husk optimized using Taguchi method (Srivastava et al. 2008).

In the present work, the removal of copper ions from aqueous solution was evaluated using the synthesized magnetic nanoparticles immobilized on AC. In addition, the effect of three parameters, including the concentration of Cu(II), dosage of Fe3O4/AC novel nanocomposite and pH on the removal of Cu(II) using Fe3O4/AC nanocomposite were studied. The Taguchi design was used to optimize various variables of pH, initial concentration and nanocomposite dosage (Fe3O4/AC) affecting the adsorption of Cu(II) from aqueous solution.

MATERIALS AND METHODS

Materials

Copper nitrate, ferric sulfate, ferric chloride, ammonium hydroxide, hydrochloric acid, sodium hydroxide, and AC were obtained from Merck (Germany). The pH was adjusted using HCl and 0.1 M NaOH.

Preparation and characterization of Fe3O4/AC

Aqueous coprecipitation under alkaline conditions has been used to prepare nanoparticles with homogeneous composition and narrow size distribution (Laurent et al. 2008). FeSO4.7H2O of 2.1 g, FeCl3.6H2O of 3.1 g, and AC of 10 g were dissolved under inert atmosphere in 80 ml of double distilled water with vigorous stirring. While the solution was heated to 80 °C, 10 ml of ammonium hydroxide solution (25%) was added and the reaction was carried out for 30 min at 80 °C under constant stirring. The resulting
suspension was allowed to cool to room temperature and then was repeatedly washed with double deionized water. The morphology and size of the bare AC and magnetic nanoparticles (Fe$_3$O$_4$/AC) were characterized by scanning electron microscopy (SEM) MV 2300 at 25 kV. Fourier transform infrared spectroscopy (FTIR) spectra of Fe$_3$O$_4$/AC nanocomposite were obtained using FTIR (Nicolet 8700, Thermo Scientific). Samples for FTIR measurement were prepared by mixing 1% (W/W) specimen with 100 mg of KBr powder and pressed into a sheer slice. A spectral resolution of 2 cm$^{-1}$ and average of 32 scans was used for each measurement.

**Adsorption experiments**

Adsorption experiments were carried out by adding different amounts of Fe$_3$O$_4$/AC nanocomposite and pollutant (Cu(II)) at a temperature of 20 ± 1 °C, an agitation rate at constant speed of 100 rpm and different pH levels. The solution was centrifuged (Kokusahin; 108 N) to separate the nanocomposite. The filtrate was analyzed using flame atomic absorption (Perkin Elmer 2380). The removal percentage of Cu(II) ions ($R_\%$) and uptake capacities ($q$) were calculated according to the following equations:

\[ R_\% = \frac{C_0 - C_e}{C_0} \times 100 \]  
\[ q = \frac{(C_0 - C_e)V}{S} \]

where $C_0$ and $C_e$ are the initial and equilibrium concentration of Cu(II) (mg L$^{-1}$), respectively, $V$ is the volume of solution (L), and $S$ is the nanocomposite mass (g).

**Design of the experiments**

Taguchi-based experimental design was used to investigate the effect of variables on characteristic properties (response) and find the optimal conditions of factors using Minitab 16 statistical software (Version 1.1). It is possible to determine the optimal experimental conditions with the least variability. However, conventional statistical experimental designs offer the optimal conditions on the basis of the measured values of the characteristic properties. This ability is one of the advantages of the Taguchi method over the conventional experimental design methods. The variability is expressed by signal-to-noise ratio (S/N) (Moghaddam et al. 2012).

Preliminary tests were performed and significant factors affecting the Cu(II) removal were identified as initial concentration of Cu(II), Fe$_3$O$_4$/AC nanocomposite dosage, temperature, pH and time. The most significant factors were chosen for optimization. The three selected factors, including the amount of nanoparticles, initial concentration of Cu(II), and pH are considered as the main variables, and each of the factors have three levels.

According to the classical full factorial design $3^3$ (= 27) experiments required to consider the influencing parameters. In the Taguchi experimental design method, OAs are used to obtain the necessary experiments. The involved factors and their levels are shown in Table 1. Concerning the three factors and three levels for each, a proper OA should be chosen. The degree of freedom for each factor is 2, therefore the total degree of freedom will be 6. Considering that, the proper OA will be $L_9$ and is shown in Table 2. Each line of this table shows an experiment, thus nine experiments are necessary. In order to reduce error, each experiment was repeated twice.

Analysis of variance (ANOVA) is a statistical method that can determine the significance and contribution percentage of any variable parameters. ANOVA is a powerful statistical method that can separate and estimate the

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Factors and their levels which were studied by Taguchi method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>Level 1</td>
</tr>
<tr>
<td>(A) pH</td>
<td>7.0</td>
</tr>
<tr>
<td>(B) Fe$_3$O$_4$/AC dosage (g L$^{-1}$)</td>
<td>0.1</td>
</tr>
<tr>
<td>(C) Initial concentration of Cu(II) (mg L$^{-1}$)</td>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>OA of $L_9$ for designing experiments by the Taguchi method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of OAs</td>
<td>pH of solution</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
</tr>
</tbody>
</table>
source and reason of each variable; therefore, the optimum levels of these factors could be obtained. The contribution of each factor has been calculated using ANOVA.

RESULTS AND DISCUSSION

Morphological analysis

Representative SEM images are shown in Figure 1. SEM analysis revealed that the surface of AC was not uniform (Figure 1(a)). Many pores were found on the surface of the AC (Figure 1(a)). Fe₃O₄ nanoparticles of 20–50 nm in diameter were observed on the surface of the AC as revealed by Figure 1(b). It is clear that the Fe₃O₄/AC are essentially monodispersed and have a similar mean diameter of 34 nm (Figure 1(a)). Also, aggregation of Fe₃O₄ particles was not observed which indicated that aggregation of Fe₃O₄ nanoparticles was well controlled by the presence of the AC.

Coprecipitation in aqueous solution, which is probably the most common and efficient method to obtain magnetic particles, was used to prepare Fe₃O₄/AC (Laurent et al. 2008). The synthesized magnetic nanoparticles (Fe₃O₄) using this method immobilized on AC have more narrow size distribution (Liu et al. 2013). The FTIR spectra in the wave numbers ranging from 400 to 4,000 cm⁻¹ regarding Fe₃O₄/AC nanocomposite are presented in Figure 2. As shown in Figure 2, there is wide and large absorption band around 3,396 cm⁻¹, which is mainly caused by the adsorbed water on the surface and stretching vibration of O–H in the H₂O (Yang et al. 2010). The absorption peaks were observed at the bands around 668, 470 and 791 cm⁻¹ corresponding to Fe–O stretches of Fe₃O₄ which were observed in Figure 2 (Mansouriieh et al. 2011). The appeared peak around

Figure 1  |  SEM image of (a) AC and (b) Fe₃O₄/AC nanocomposite.
The various vibrations of -CH₂ and -CH₃ groups (Panneerselvam et al. 2014). While the presence of peaks at 1,627 cm⁻¹ and 1,045 cm⁻¹ are ascribed to the C=O stretch vibration, and aliphatic C–N stretching of the AC, respectively (Liu et al. 2015). These results confirmed the Fe₃O₄/AC nanocomposite formation.

### Designing the experiment Cu(II) removal using Fe₃O₄/AC nanoparticles based on the features of OAs

To optimize the conditions of the process, the S/N method was used. In this method, the signal and noise represent the desirable and undesirable values for the output characteristic, respectively. The use of the loss function is suggested by Taguchi method to evaluate the performance characteristic deviating from each desired value. By using the value of this function, which is further transformed to a S/N ratio, one can determine the level of factors and their effectiveness. Normally, three different categories of the performance characteristic (including the lower, the better; the higher, the better; and the nominal, the better) are used in the S/N ratio analysis (Moghaddam et al. 2015). In this study, ‘the higher, the better’ quality characteristics were used. The values of the S/N ratio were substituted into Equation (3) and are shown in Table 3. When the bigger characteristic is better, the S/N ratio is defined as (Sheidaei & Behnajady 2014):

$$\frac{S}{N} = -10\log \left( \frac{1}{n} \sum_{i=1}^{n} \frac{1}{y_i^2} \right)$$  \hspace{1cm} (3)

where $y_i$ is the characteristic property and $n$ is the number of replications in the experiment. The results of the experiments are shown in Table 4. The standard deviation and variance indicate that the data distribution is close to normal. In the Taguchi method, the more the proportion of S/N on a level, the more appropriate that level of the factor. Based on S/N results shown in Table 5, the optimum conditions in the process of Cu(II) removal from aqueous solutions using Fe₃O₄/AC nanocomposite is shown in Table 6.

Table 3 | L₉ OA (levels of three different factors and obtained results)

<table>
<thead>
<tr>
<th>Experiment no.</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>R1%</th>
<th>q</th>
<th>S/N ratio</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7</td>
<td>0.1</td>
<td>10</td>
<td>99.36</td>
<td>9,940</td>
<td>29.954</td>
<td>99.46</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>0.2</td>
<td>15</td>
<td>98.43</td>
<td>7,382.5</td>
<td>39.8317</td>
<td>98.09</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>0.5</td>
<td>20</td>
<td>97.84</td>
<td>3,913.6</td>
<td>39.8330</td>
<td>98.09</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0.1</td>
<td>15</td>
<td>99.23</td>
<td>14,885</td>
<td>39.9555</td>
<td>99.48</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>0.2</td>
<td>20</td>
<td>98.40</td>
<td>9,839.5</td>
<td>39.8680</td>
<td>99.18</td>
</tr>
<tr>
<td>6</td>
<td>8</td>
<td>0.5</td>
<td>10</td>
<td>96.84</td>
<td>1,936.8</td>
<td>39.6093</td>
<td>96.50</td>
</tr>
<tr>
<td>7</td>
<td>9</td>
<td>0.1</td>
<td>20</td>
<td>98.94</td>
<td>19,778</td>
<td>39.8766</td>
<td>98.60</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
<td>0.2</td>
<td>10</td>
<td>97.14</td>
<td>4,866</td>
<td>39.6100</td>
<td>95.61</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>0.5</td>
<td>15</td>
<td>95.17</td>
<td>2,855.2</td>
<td>39.5781</td>
<td>95.25</td>
</tr>
</tbody>
</table>

Figure 3 shows the effect of different parameters on the amount of S/N. As shown in Figure 3, the maximum S/N is obtained with pH = 7, nanocomposite dosage of 0.1 g L⁻¹ and initial Cu(II) concentration of 20 mg L⁻¹. The average effect of each factor on response surface data is as shown in Figure 4. As shown in Figure 4, the average maximum is located for pH and dosage at the lowest level and for the initial concentration of Cu(II) at the highest level.
ANOVA

The ANOVA results and the contribution percentages of each factor are shown in Table 7 and Figure 5. The degree of freedom (df) for each factor was 2 and the total df was 6. Since the df for the error term was 0, the variance for the error term could not be attained. Results obtained from Table 7 show that the $F$-values for all the factors are less than the $F$-values derived from the statistical table ($F_{\text{statistical table}} = 5.14$) in 95% level of confidence, thus each factor is significantly effective.

According to the results in Figure 5, nanocomposite dosage (B) has the greatest effect (52.38%), followed by the pH (36.2%) and initial concentration of Cu(11.4%). From the calculated $F$-ratios, it can be concluded that the parameters are statistically significant at 95% confidence level. Thus dosage (B) is the most important parameter in the process of Cu(II) removal and the highest efficiency was obtained at pH = 7.

Multi-response optimization using Taguchi method

The removal efficiency in Tests 1 to 9 measured for Cu(II) is shown in Table 4 by substituting the number of experimental repetitions and results of the measurement ($R$%) into Equation (1). Ranks of three factors for two responses, removal ($R$) and capacity uptake ($q$) of Cu(II) are provided in Table 3. According to the results in Table 3, the efficiency of Cu(II) removal is affected by the initial Cu(II) concentration, thus the removal percentage increased as Cu(II) concentration increased. This was probably the result of a higher mass transfer driving force from the increase in the number of molecules competing for the available binding sites on the adsorbent as the initial concentration of Cu(II) increases (Fan et al. 2011).

The effect of pH solution on Cu(II) removal shows that the optimum pH for Cu(II) removal is found at pH = 7. Cu(II) in aqueous solution can be present in several forms, such as Cu(II), Cu(OH)$^+$, Cu(OH)$_2$, Cu(OH)$_2$, Cu(OH)$_3^-$, and Cu(OH)$_3^2^-$. Cu(II) is the predominant species at pH < 6 (Sheng et al. 2010). The smaller removal and adsorption capabilities of Fe$_3$O$_4$/AC at lower pH levels, are probably due to the significant competition between Cu(II) and hydrogen ions for adsorption sites. Furthermore, Cu(OH)$_{15}^-$ and Cu(OH)$_{16}^2^-$ and nanocomposite surface negative charge repulsion forces at pH > 7 reduce the metal ion removal and adsorption using Fe$_3$O$_4$/AC nanocomposite (Repo et al. 2011).

Although the Cu(II) removal percentage decreased with an increase in the adsorbent dosage, this decrease could be as a result of the aggregation at the nanocomposite surface and an increase in diffusion path length (Gonen & Serin 2012).

CONCLUSIONS

This study synthesized the magnetic nanoparticles immobilized on the AC via coprecipitation in aqueous solution. FTIR results confirmed Fe$_3$O$_4$/AC nanocomposite
Prepared monodispersed Fe$_3$O$_4$/AC with an average particle diameter of 34 nm, was used for Cu(II) removal from aqueous solution. Taguchi statistical design with OA is efficiently used to optimize Cu(II) removal from aqueous solution and evaluate the effect of different parameters of pH, dosage, and concentration. Applying this simple optimization method showed that the most important factor affecting the Cu(II) removal was the dosage of adsorbent (52.58%). Batch removal experiments showed that the optimized pollutant removal can be
achieved at pH 7, nanocomposite dosage of 0.1 g L\(^{-1}\) and initial concentration of 20 mg L\(^{-1}\) at constant temperature of 25 °C. Cu(II) removal percentage using Fe\(_3\)O\(_4\)/AC reached 99.8% after 10 min in the optimum condition.

Finally, it could be concluded that, due to the ease of the green synthesis route for the preparation of Fe\(_3\)O\(_4\)/AC, utilization of the Taguchi method with fewer experiments is a suitable approach for optimization of the removal process. However, effectiveness of adsorbent with 99.8% Cu(II) removal, has huge implications for effective inorganic pollutant removal from water.

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