# Adsorptive removal of azide ion from aqueous solutions using modified activated carbon magnetic nanocomposite

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**Abstract**

In this work, the activated carbon/magnetic $Fe_3O_4$ nanocomposite was synthesized and characterized by TEM and XRD measurements. This magnetic nanocomposite was modified with cetylpyridinium chloride (CPC) and thus used as a new adsorbent for removal of azide ion from an aqueous solution. In an aqueous solution of azide ion, the adsorption capacity was evaluated using both the Langmuir and Freundlich adsorption isotherm models. The main factors affecting the removal of azide ion, such as pH of solution, dosage of adsorbent, surfactant amount and contact time have been investigated in order to find the optimum adsorption conditions. The experimental data were analyzed by the Langmuir and Freundlich adsorption models. Equilibrium data fitted very well with the Langmuir model and the maximum predicted adsorption capacities ($q_{max}$) was found to be 22.22 mg $g^{-1}$. It was shown that the sorbent can remove more than 95% of azide ion within the first 20 min of contact time. The results indicated that the modified magnetic nanocomposite can be successfully employed in removal of azide ion from water samples.

**Keywords:** Azide ion; Removal; Adsorption isotherm; $Fe_3O_4$ nanoparticle; Magnetic nanocomposite.

## 1. Introduction

Azide compounds contain three nitrogen atoms connected to each other ($-N=N^+=N^-$). These compounds are classified to inorganic and organic azides. In organic azides, the three nitrogen atoms are connected to a carbon atom and in inorganic azides the are connected to a metal such as sodium ($NaN_3$) or lead ($Pb(N_3)_2$) [1]. Azides are widely used for a variety of technological applications including agriculture in the production of pesticides and herbicides, biomedical sciences as preservative in diagnostic reagents, the car industry as a propellant for air bags, and for the production of detonators and other explosives for military purposes [2]. Azides are highly toxic and can be incorporated into the body by breathing vapor and dust containing azides, by skin contact mainly with solution, vapor and food containing azide [3,4]. Therefore, much attention has been paid to azides treatment before the discharge of wastewaters.

Based on literature survey, the removal of azide ions from aqueous solutions was carried out by several methods. In the first method, azide ion was removed via reduction of azide ions by hydrogen gas in the presence of nickel catalyst according to following equation [5]:

$$N_3^- + H_2 + H_2O \rightarrow NH_3 + N_2 + OH^- \qquad (1)$$

This process was performed at a temperature between +5 °C and +40 °C. The applied pressure was between the atmospheric pressure and 60 bar. In other method, azide ion was removed by electrochemical decomposition of azide ion in an electrolyzer which contained one or more cell units [6]. Ozonation was used for removal of azide compounds from gaseous and aqueous wastes [7]. In this process, the alkali metal azides were oxidized by ozone gas to nitrogen and alkali metal nitrate. This process was carried out at a low pH 10. In other process, the sodium azide was removed by reaction with sodium nitrite in the presence of sulfuric acid as follow [8]:

$$2NaNO_2 + H_2SO_4 \longrightarrow 2HNO_2 + Na_2SO_4 \qquad (2)$$
$$2NaN_3 + 2HNO_2 \rightarrow 3N_2 + 2NO + 2NaOH \qquad (3)$$
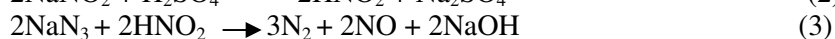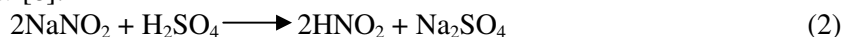
This process is carried out in a hood due to the formation of nitric oxide. To the best of our knowledge, there is no report about application of sorbents for adsorptive removal of azides.

The most widely used and effective physical method for adsorption in industry is activated carbon [9-11]. Unfortunately, activated carbons are notoriously difficult to separate from solution. Therefore, during conventional adsorption process, high speed centrifugation or filtration is inevitable to separate adsorbent from solution after adsorption, which greatly reduces the operating efficiency [12-15]. The application of magnetic adsorbents, which contain magnetic cores to ensure magnetic separation and functionalized shells to provide favorable functional groups for adsorption, can solve this problem. Attempts to use magnetic separation by applying an appropriate magnet have been reported for nanoparticles iron oxide or cobalt incorporated in mesoporous silica and carbon [16-19]. A nanocomposite is a matrix to which nanoparticles have been added to improve a particular property of the material. Carbon nanocomposites have received more attention in the recent years in view of their special properties such as high specific surface ares and thermal and mechanical stability. Magnetic carbon nanocomposites (MCNCs) combining magnetic properties and the superior adsorption capability can play an enormous role in environmental remediation. Magnetic carbon nanocomposites were synthesized and used recently [20,21]. It can be easily separated from the solution by an external magnet.

In the present work, activated carbon/magnetic $Fe_3O_4$ nanocomposite were employed for removal of azide ion and used as an effective adsorbent in the wastewater treatment. The technique was found to be very useful and cost-effective for a removal of azide ion. This is the first report in the application of magnetic sorbent for azide removal from water samples.

## 2. Materials and Methods

### 2.1. Reagents
All the chemicals and reagents used in this work were of analytical grade and purchased from Merck (Merck, Darmstadt, Germany). Deionized water was used throughout the study. A stock solution (1000 µg mL$^{-1}$) of azide ion was prepared by dissolving 0.1548 g of sodium azide ion in deionized water and diluting to 100 mL in a volumetric flask. More diluted solutions were prepared using this stock solution. A 1.0 M copper nitrate solution was prepared by dissolving by dissolving 24.16 g Cu(NO$_3$).3H$_2$O in water and diluting to 100 mL in a volumetric flask. The acetate buffer solution (pH 5.8) was used to adjust the pH.

### 2.2. Instrumentation
A Hitachi model 3310 UV-Vis spectrophotometer with 1-cm quartz cells was used for determination of azide ion concentration in the solutions. A Metrohm model 713 pH-meter was used for pH measurements. The size and structure of the nanoparticles were characterized by transmission electron microscopy (TEM, CM 10, 100 KV, Philips, Netherland).

### 2.3. Synthesis of activated carbon/magnetic Fe₃O₄ nanocomposite
For synthesis, firstly, the activated carbon was modified with nitric acid (63%) for 3 h at 80 °C to make it hydrophilic. Then 1.0 g of the hydrophilic activated carbon was dispersed in 100 mL aqueous solution containing 2.98 g FeCl$_3$·6H$_2$O and 1.53 g FeSO$_4$·7H$_2$O at 70 °C under N$_2$ condition. NaOH solution (30 mL, 0.5 mol L$^{-1}$) was added dropwise to precipitate iron oxides. After the addition of NaOH solution, the mixture was adjusted to pH 11 and stirred for 1 h. The mixture was aged at 70 °C for 2 h and was washed 3 times with doubly distilled water. The precipitate was dried in an oven at 100 °C for 1 h.

### 2.4. Preparation of CPC coated activated cabon/magnetic Fe₃O₄ nanocomposite
For coating the magnetic composites, 50 mg activated carbon/magnetic Fe$_3$O$_4$ nanocomposite was added to 2.5 mL of 1.0 % (w/v) CPC solution in a beaker. The solution was shaken for 1 min on the shaker. Then, CPC-coated activated carbon/nano-Fe$_3$O$_4$ composites (CPC/AC/nano-Fe$_3$O$_4$) was separated using the magnet and washed with distilled water for several times.

### 2.5. Spectrophotometric determination of azide ion
A simple spectrophotometric method based on complex formation of azid ion with Cu$^{2+}$ ion (CuN$^+$) in acetate buffer media was used for monitoring azide ion removal [22]. In this work, an aliquot of the azide ion solution with a concentration in the range of 1.0-25 µg mL$^{-1}$, 1.0 mL of 1.0 M Cu$^{2+}$ ion solution and 1.0 mL of acetate buffer solution (pH 5.8) was transferred into a 10-mL volumetric flask and diluted with distilled water and the absorbance was measured at 365 nm.

### 2.6. Removal of azide ion on CPC/AC/nano-Fe₃O₄ composite
A batch procedure was carried out for the removal process. At first, 25 mL solution with different concentrations of azide ion,was poured into a beaker and the pH of the solution was adjusted at 6.0 using 0.1 mol L$^{-1}$ HCl and/or 0.1 mol L$^{-1}$ NaOH. Then, 50 mg CPC/AC/nano-Fe$_3$O$_4$ composite was added and the solution was stirred for 20 min. Then, azide ion loaded nanoparticles were separated using a strong magnet (1.2 Tesla). The concentration of azide ion in the stripped solution was measured spectrophotometrically according to section 2.4 (Fig. 1). After decanting the supernatant solution, the collected magnetic nanocomposites was washed with 0.5 mL of 1.0 mol L$^{-1}$ NaOH solution for reuse. The entire scheme of the removal procedure is shown in Scheme 1.
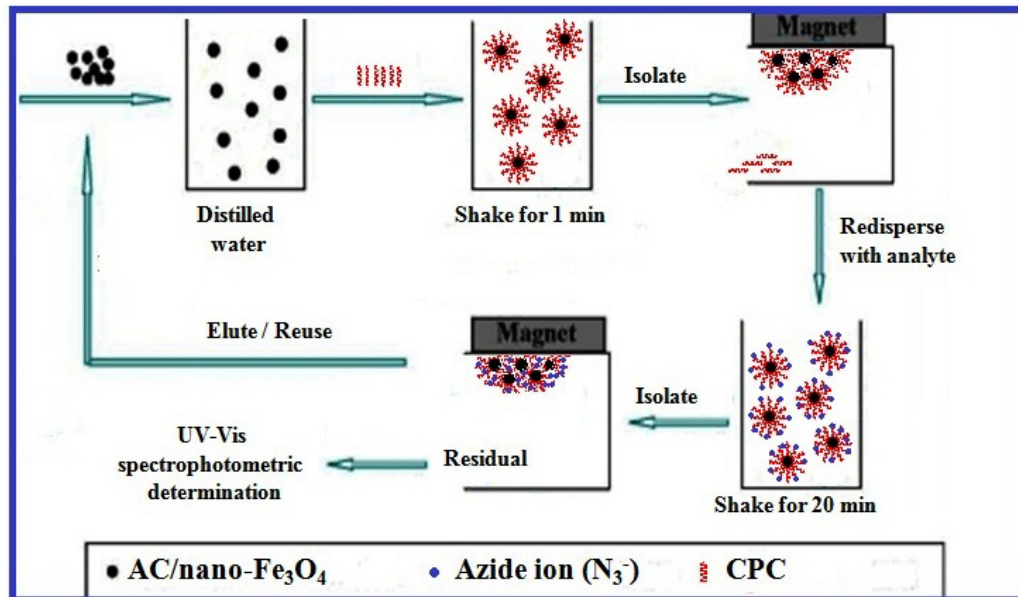
**Scheme 1.** Scheme illustrating the steps involved in removal of azide ion from aqueous solutions by using CPC/MWCNT/Nano-Fe$_3$O$_4$ composites

## 3. Results and Discussion

### 3.1. Characterization of the adsorbent

The size and size distribution of Fe$_3$O$_4$ magnetic nanoparticles were characterized by TEM image (Fig. 2). As can be observed, the particles are nearly spherical in shape, and have uniform distribution of particle size in the range 30-50 nm, and carbon atoms are surrounding Fe$_3$O$_4$ nanoparticles and almost a uniform image of nanocomposite can be observed in a large scale. No obvious large size of iron oxide was detected.
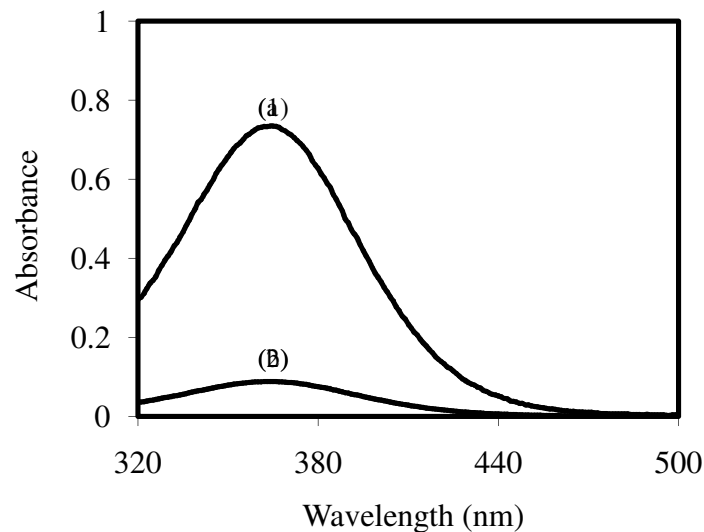


**Figure 1.** Absorption spectra of the complex of azide ion with Cu$^{2+}$ ion in acetate buffer a) before adsorption b) after adsorptive removal by CPC/AC/nano-Fe$_3$O$_4$ composite. Conditions: Azide ion, 20 µg mL$^{-1}$; Cu$^{2+}$, 0.10 M; pH 5.8.

### 3.2. Effect of pH

The effect of pH on the removal of azide ion in the range 2.0–9.0, was investigated using 0.01 mol L$^{-1}$ HCl or NaOH solutions for pH adjustment, with the initial azide ion concentration fixed at 20 µg mL$^{-1}$. The percent adsorption increased by increasing pH and reached maximum at pH 6.0, and decreased at higher pH values (Fig. 3). Thus pH 6.0 was selected for future studies. Lower removal at pH values higher than 6.0 can be due to the competition of OH$^-$ ion with azide ion in the adsorption on the adsorbent.
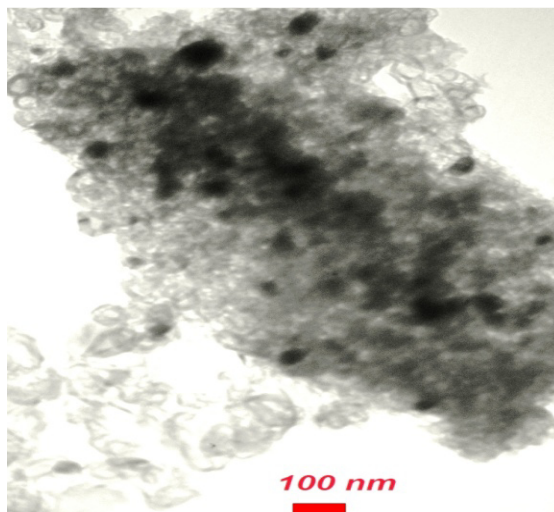
**Figure 2.** TEM image of activated carbon/magnetic $Fe_3O_4$ nanocomposite.

### 3.3. Effect of CPC concentration

It was observed that magnetic nanocomposites without modification did not adsorb azide ion from aqueous solution, while magnetic nanocomposites modified by CPC adsorbed azide ion efficiently. The suggested mechanism for the adsorption of the azide ion by magnetic nanocomposites modified by CPC is due to that cetyl pyridinium choloride (CPC) is a cationic quaternary ammonium surfactant and tends to interact with surface magnetic nanocomposite via hydrophobic chains and coats them and hydrophilic ammonium group in CPC adsorb azide ion in solution. The influence of CPC amount in modification of activated carbon magnetic nanocomposite on the removal efficiency was studied in the range 1.0-5.0 mL of 1.0 % (w/v) CPC under optimal conditions of other variables. The results revealed that by increasing the amount of surfactant up to 2.5 mL, the efficiency of removal of azide ion was increased and then remained nearly constant. Therefore, 2.5 mL of 1.0 % (w/v) solution of CPC was chosen as the most suitable concentration of CPC for further experiments.
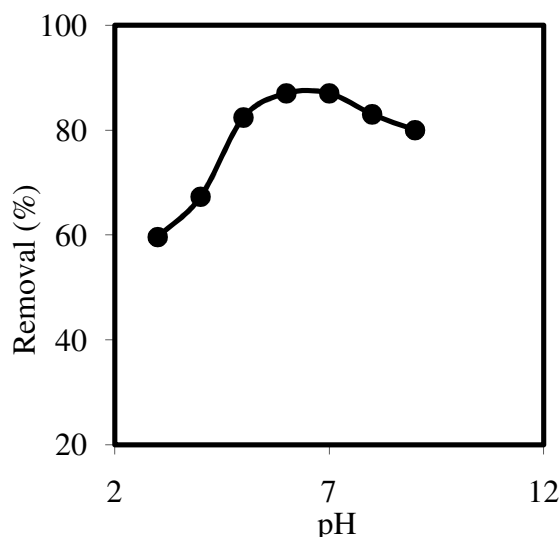


**Figure 3.** Effect of pH on removal efficiency of azide ion. Conditions: 25 mL of 20 μg mL$^{-1}$ of azide ion solution; 50 mg magnetic nanocomposite; shaking time, 20 min.

### 3.4. Effect of amount of adsorbent

The effect of different amounts of CPC/AC/nano-$Fe_3O_4$ composite on the adsorption of azide ion was studied to determine the optimum amount for removal of azide ion a 25 mL of 20 μg mL$^{-1}$ of azide ion solution at pH 6.0. As Fig. 4 shows the removal percentage of azide ion increased by increasing the amount of adsorbent up to 50 mg and remained nearly constant at higher values. Therefore, a 50 mg of adsorbent was used as optimal value.
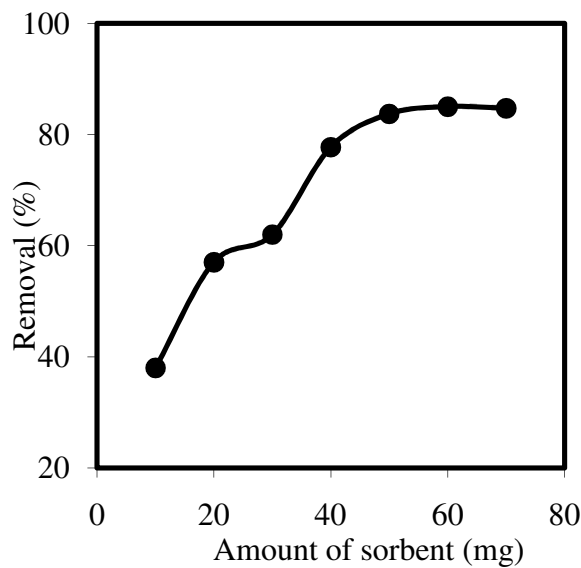
**Figure 4.** Effect of amount of magnetic nanocomposite on adsorption efficiency of azide ion. Conditions: 25 mL of 20 µg mL$^{-1}$ of azide ion solution; pH 6.0, shaking time, 20 min.

### 3.5. Effect of shaking time

The effect of shaking time on the adsorption of azide ion was studied to determine the optimum time needed for removal of azide ion in solution by CPC/AC/nano-Fe$_3$O$_4$ composite . A 50 mg of adsorbent was added into a 25 mL of 20 µg mL$^{-1}$ of azide ion solution at pH 6.0, and removal percentage with shaking time was monitored. The results are shown in Fig. 5. The decrease in the concentration of azide ion with time is due to its adsorption on adsorbent. It can be seen that in about 20 min, almost all the azide ion is adsorbed. Agitation time of 20 min was selected as optimum time for adsorption.
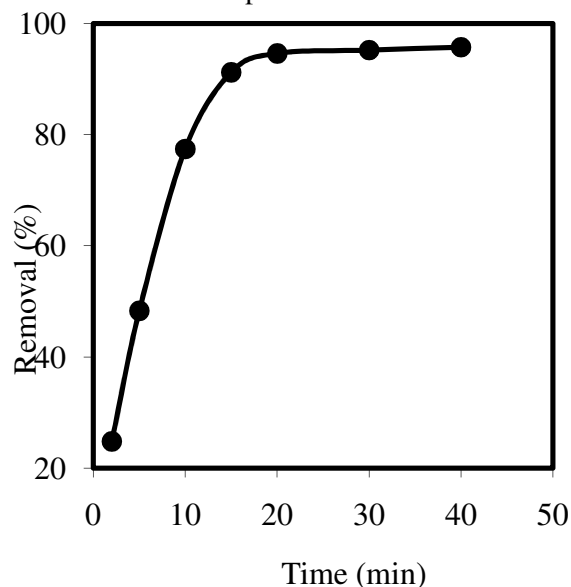


**Figure 5.** Effect of shaking time on removal efficiency of azide ion. Conditions: 25 mL of 20 µg mL$^{-1}$ of azide ion solution; 50 mg magnetic nanocomposite; pH 6.0.

### 3.6. Adsorption isotherm model analysis

Equilibrium adsorption isotherm model which is the number of mg adsorbed per gram of adsorbent ($q_e$) vs. the equilibrium concentration of adsorbate is fundamental in describing the interactive behavior between adsorbate and adsorbent. Analysis of isotherm data is important for predicting the adsorption capacity of the adsorbent, which is one of the main parameters required for the design of an adsorption system. Equilibrium isotherm studies were carried out with different initial concentrations of azide ion (10–500 µg mL$^{-1}$) at 25 °C and at pH 6.0. Both Langmuir and Freundlich adsorption isotherms were used to normalize the adsorption data

Langmuir adsorption isotherm is based on the physical hypothesis that the maximum adsorption capacity consists of a monolayer adsorption, that there are no interactions between adsorbed molecules, and that the adsorption energy is distributed homogeneously over the entire coverage surface [23-26]. The linearized Langmiur isotherm Eq. (4) can be expressed as follows:

$$\frac{C_e}{q_e} = C_e \left(\frac{a_L}{K_L}\right) + \left(\frac{1}{K_L}\right) \tag{4}$$

where $C_e$ is the equilibrium concentration of azide ion in the solution ($\mu g\ mL^{-1}$), $q_e$ is the amount of azide ion adsorbed per unit mass of adsorbent (mg $g^{-1}$). At equilibrium concentration, $C_e$, $a_L$ (L $mg^{-1}$) and $K_L$ (L $g^{-1}$) are the Langmuir constants with $a_L$ related to the adsorption energy and $q_m$ [$=K_L/a_L$] signifies the maximum adsorption capacity (mg $g^{-1}$), which depends on the number of adsorption sites. The values of $a_L$ and $K_L$ are calculated from the slope and intercept of the plot of $C_e/q_e$ vs. $C_e$ (Fig. 6). The amount of azide ion adsorbed (mg $g^{-1}$) was calculated based on a mass balance equation as given below:

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{5}$$

where $C_0$ is the initial concentration of azide ion in $mgL^{-1}$, $V$ is the volume of experimental solution in litter, and $m$ is the dry weight of nanoparticles in gram. The parameters of the Langmuir equation were calculated and are given in Table 1. Based on this table, the maximum adsorption capacity of nanoparticles ($q_m$) is 22.22 mg $g^{-1}$.
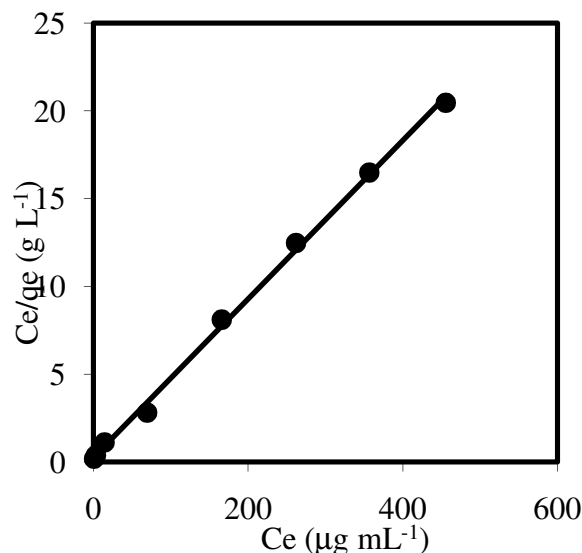


**Figure 6.** Linearization of the Langmuir isotherm. Conditions: 50 mL of 20 $\mu g\ mL^{-1}$ of azide ion solution; 50 mg magnetic nanocomposite; pH 6.0, shaking time, 20 min.

The linearized form of the Freundlich adsorption isotherm equation is:

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \tag{6}$$

where $C_e$ is the equilibrium concentration (mg $L^{-1}$), $q_e$ is the amount adsorbed at equilibrium (mg $g^{-1}$), and $K_f$ ($mg1^{-1/n}\ L^{1/n}\ g^{-1}$) and $1/n$ are Freundlich constants depending on the temperature and the given adsorbent–adsorbate couple, $n$ is an empirical parameter related to sorption, and $K_f$ indicates the adsorption capacity. These values ware calculated from the intercept and slope of the plot of $\ln q_e$ vs. $\ln C_e$, that listed in Table 1. The adsorption process is better fitted with the Langmuir isotherm model ($R^2 > 0.998$), which indicated the homogeneous distribution of active sites on the surface of CPC/AC/nano-$Fe_3O_4$ composite.

**Table 1.** Parameters of Langmuir and Freundlich isotherm equations, regression coefficients (r) for the adsorption of azide ion on proposed magnetic adsorbent under optimum conditions.

| Langmuir | $a_L$(L$mg^{-1}$) | $k_L$(L$g^{-1}$) | $k_L/a_L$[$=qm$](mg$g^{-1}$) | $R_L$* | r |
|---|---|---|---|---|---|
| | 0.11 | 2.38 | 22.22 | 0.18 | 0.999 |
| Freundlich | | | $k_F$(mg$^{1-1/n}$ L$^{1/n}$ g$^{-1}$) | $1/n$ | r |
| | | | 5.66 | 0.2278 | 0.974 |

### 3.7. Regeneration and reuse of the adsorbent

In order to evaluate the possibility of regeneration and reuse of the magnetic nanocomposite adsorbent, desorption experiments were performed on adsorbent. Azide desorption from CPC/AC/nano-$Fe_3O_4$ composite was conducted by washing the azide ion located on adsorbent using solutions at various pH values. It was observed that azide ion desorption increases with increasing of pH and at pH= 9.0 up to 95% removal is achieved. Results show that the azide ion adsorbed by the magnetic nanocomposite could be easily desorbed, and thereby activated carbon/ magnetic $Fe_3O_4$ nanocomposite can be employed repeatedly in wastewater management. The reusability of the sorbent was greater than 5 cycles without any loss in its sorption behavior. Therefore, the magnetic nanocomposite can be a good reusable and economical sorbent.

## Conclusion

Azide ion is an anion that is extremely water-soluble and is a serious surface and groundwater contaminant. In this study, we prepared the CPC/AC/nano-$Fe_3O_4$ composite with a high adsorption capacity, and examined for azide ion removal. The results of this study clearly show that the adsorption isotherm data for the azide ion was derived at room temperature and treated according to Langmuir and Freundlich models. Langmuir model is almost more successful in representing experimental isotherm data for the adsorption of azide ion on magnetic nanocomposite. Also, the proposed adsorbent can be used as an effective adsorbent for rapid removal of azide ion from water. It is a good industrial candidate for removal of azide ion due to fast removal (20 min), high adsorption and good reusability.

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