

# Removal of Phosphate from Aqueous Solutions by Iron Nano-Magnetic Particle Coated with Powder Activated Carbon

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## Abstract

**Background:** The increase in the amount of phosphate in aquatic environments disrupts the balance of the growth of aquatic organisms and causes serious environmental problems. The aim of this study is to investigate the removal of phosphate ion using powdered activated carbon coated with magnetic iron nanoparticles.

**Methods:** For this purpose, the synthesis of nanoparticles was carried out through co-precipitation mechanism and the effects of various parameters including the amount of adsorbent dose, pH, initial concentration, temperature, contact time, and also the effect of interaction ions on adsorption performance were evaluated in a batch system. Then, the study of Kinetics and isotherms was performed on the obtained data. To determine the characteristics of the produced nanoparticles, scanning electron microscopy, X-ray Diffraction and infrared spectroscopy were used.

**Results:** The results showed that the maximum adsorption (100%) happened in pH=4 after 90 min of the contact between the solution and the adsorbent. experimental data also matched the Langmuir isotherm.

**Conclusions:** According to the results obtained, as an eco-friendly adsorbent, the powdered activated carbon sorbent coated with magnetic iron nanoparticles has a desirable capability in removal of phosphate.

**Keywords:** Phosphate; Adsorption; Powdered activated carbon; Iron magnetic nanoparticles

## 1. Introduction

Phosphorus is an important component of sewage. It can be seen in the wastewater in various forms, such as organic compounds, polyphosphates and Ortho-phosphates (1). 50 to 70 percent of the sewage phosphorus is in the form of orthophosphate (2). Phosphorus plays an important part as an essential substance for the growth of plants in soil and as a limiting element in the growth of algae and production of eutrophication in surface water bodies (3, 4). Since 1970, the increase in the disposal of sewage into receiving waters, has announced phosphorus as an important pollutant in the creation of the eutrophication phenomenon and destruction of receiving waters (2). Sewage and agricultural wastewaters have a phosphorus concentration between 15 and 2,000 mg/L (5, 6) while for the emergence of the

eutrophication phenomenon a concentration of 0.005 to 0.05 mg/L of phosphate in terms of phosphorus is needed (7). Phosphate standard in drinking water is 0.2 mg/L (8) and effluent standard for discharge to surface waters is 6 mg/L (9). Removal of phosphate from sewage is an effective way to control eutrophication. Therefore, to get to a lower level than the standard, there are various methods for removing phosphate from aqueous environments, including the process of adsorption, chemical precipitation, ion exchange, biological methods, crystallization, and reverse osmosis (RO)(4, 10, 11). Surface adsorption process is a suitable method for removing phosphate from aqueous environments, where the substance adsorption capacity is increased by using surface activation (12, 13). Nowadays, the use of nano-adsorbents for the removal of pollutants has

been taken into consideration and is being widely used. Relative to their volumes, nanoparticles create a significant surface, which thus increase the dynamic capacity of the adsorbent and do the quick removal with a very high degree of efficiency (14). With regard to the possibility of their easy separation by using external magnetic field, iron oxide nanoparticles can be used as adsorbents in water treatment process. Considering the unique properties of iron nanoparticles and the availability and cost-effectiveness of activated carbon, this study aims to synthesize powdered activated carbon coated with magnetite nanoparticles, and to evaluate its efficacy in the removal of phosphate from aqueous solutions.

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## 2. Methods

### 2.1. Preparation of nanoparticles

The method of magnetic activated carbon nanoparticle synthesis was carried out by using the method of chemical precipitation by adding divalent and trivalent iron salts in an alkaline environment and by blowing nitrogen gas for deoxygenation. Then, SEM and FTIR tests were used to determine the structure and morphology of the adsorbent surface and to determine the functional groups on the adsorbent surface respectively.

### 2.2. Adsorption Study

This research was conducted discontinuously in flask with volumes of 100 ml. The stock solution 100 mg/L of potassium hydrogen diphosphate was used to prepare the concentrations under study by diluting a certain volume of the stock solution with double-distilled water. For doing the tests, first 50 ml of a sample with certain concentration was poured into the flask, and when needed, the pH was adjusted by using HCL and NaOH (1N). Then, a certain dose of adsorbent was weighed and added to the sample inside the flask and mixing took place on the shaker at different times and speeds. Various parameters such as contact time, initial pH, initial concentration of the phosphate, adsorbent concentration, and temperature were studied. Then with electromagnet N42, the nanoparticles of magnetic activated carbon was separated from the solution and Supernatant was used to measure the amount of phosphate. To ensure repeatable results, each step of the test was performed twice and the averaged results were reported. The remaining concentration of phosphate in

solution was measured based on the standard method number -P D 4500 (10, 15) at a wavelength of 690 nm and with the help of spectrophotometric device, model DR 5000 (hack long). Then different isotherms were examined.

The phosphate removal percentage was obtained by the following equation:

$$\%R = \frac{C_a}{C_0} \times 100 \quad (1)$$

Where  $C_a$  and  $C_0$  are the amount of adsorbed (difference between phosphate concentration before and after sorption) and the initial concentration of phosphate, respectively.

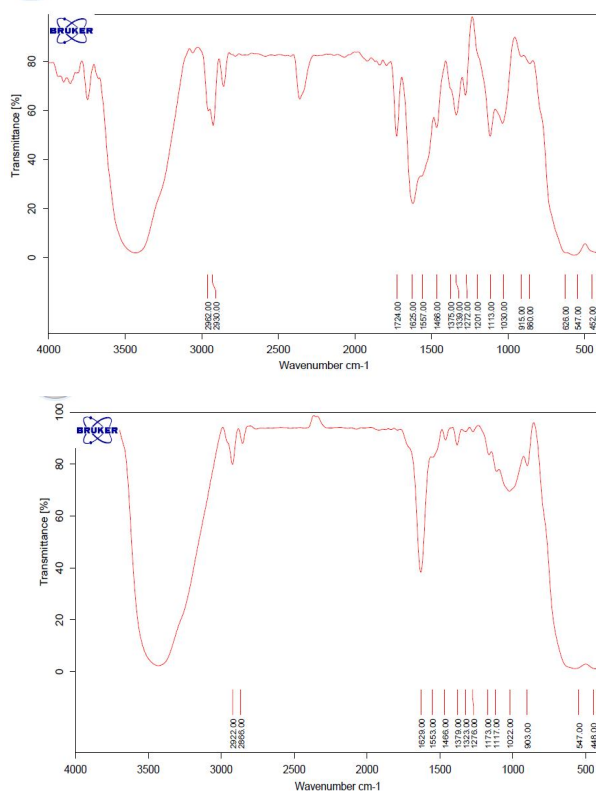
The phosphate adsorption uptake of activated carbon adsorbent ( $q_t$ ) was calculated from the following equation:

$$q_t = \frac{(C_o - C_t)V}{m} \quad (2)$$

Where  $C_o$  and  $C_t$  are the initial concentration and concentration at a time of ( $t$ ) of phosphate in terms of mg/L, respectively. Also,  $V$  is volume of the solution (L) and  $m$  is the amount of adsorbent (g).

### 2.3. Characteristics of the synthesized magnetic iron oxide nanoparticle and the activated carbon loaded with synthesized magnetic nanoparticles

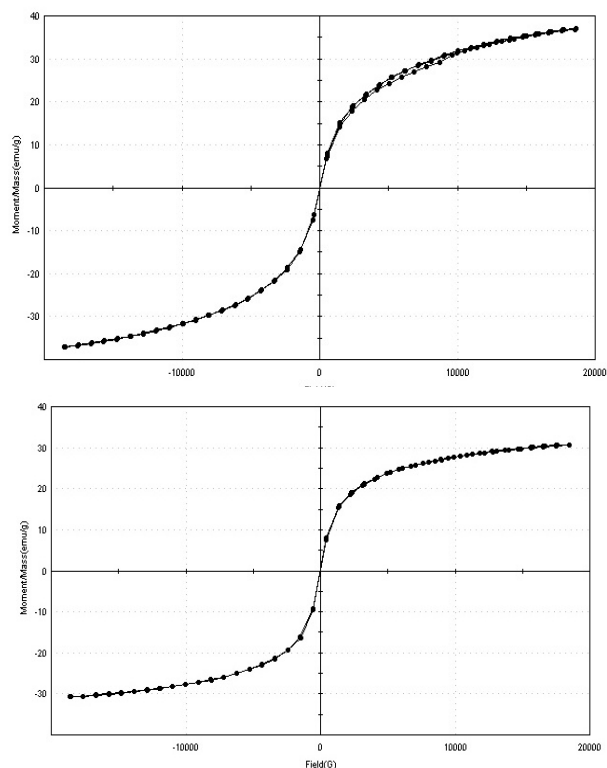
In FT-IR spectroscopic examination (Diagram 1), the existence of the peak of adsorption band of iron ferrite nanoparticles between 400 to 1000  $\text{cm}^{-1}$  is related to the links  $\text{Fe}^{2+} \leftrightarrow \text{O}$  and  $\text{Fe}^{3+} \leftrightarrow \text{O}$ , which shows the formation of  $\text{Fe}_2\text{O}_4$  or  $\text{Fe}_3\text{O}_4$  nanostructures, which proves Fe-O vibration. The peaks in the range of 1000 to 1300  $\text{cm}^{-1}$  and 2000 to 3000  $\text{cm}^{-1}$  are related to the existence of C=H and C-O stretching modes, and the peaks higher than 3000  $\text{cm}^{-1}$  are related to the existence of O-H vibrational groups in combination, all of which confirming that there are functional groups in the structure of nanoparticle. These changes in IR spectrum show that the nanoparticles have been successfully synthesized. Diagram 1 (a) is related to FT-IR spectrum of synthesized iron oxide magnetic nanoparticles and Diagram 1 (b) is about the activated carbon loaded with synthesized magnetic nanoparticles.



**Diagram 1:** (a) FTIR spectrum of the nanoparticles PAC-MNPs; and (b) FTIR spectrum of MNPs nanoparticles

#### 2.4. Magnetic properties (VSM) of synthesized magnetic iron oxide nanoparticles and activated carbon loaded with synthesized nanoparticles

The magnetic properties of nanoparticles were studied by magnetometer- vibrating sample (VSM) at room temperature. Magnetic moment versus magnetic field (ring M-H) at 300 K for magnetic nanoparticles MNPs is shown in **Diagram 2**. Magnetic curve shows that nanoparticles are super-para-magnetic and its magnetic saturation for magnetic nanoparticles is alone 37.111 emu/gr and for magnetic powdered activated carbon nanoparticles it is 30.717 emu/gr. The adsorbent synthesized in water is in dispersible way and can easily be collected by an external magnetic field within minutes. The results show that the particles have good magnetic properties and can be re-dispersed, which refers to the potential application of magnetic adsorbent.

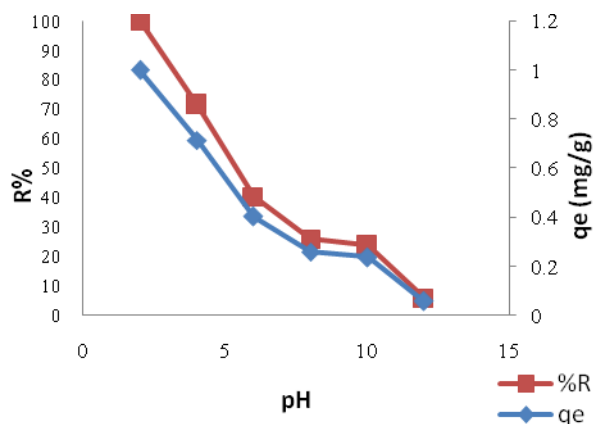


**Diagram 2:** (a) VSM curve of iron oxide magnetic nanoparticles; and (b) VSM curve related to PAC-MNPs

### 3. Results

#### 3.1. Examining the Effect of pH

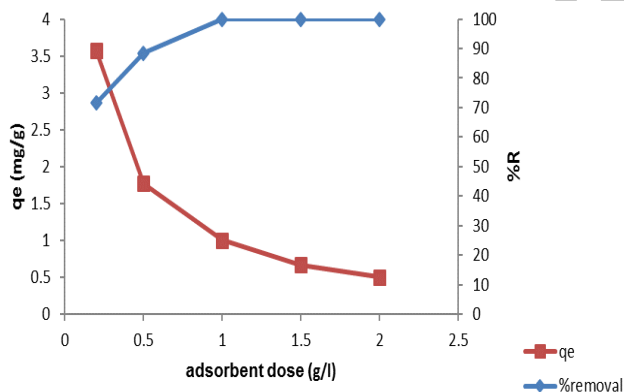
According to the results from the tests on powdered activated carbon adsorbents coated with magnetic iron oxide nanoparticles, the decrease in pH increases the efficiency of the nanoparticles (**Diagram 3**). This adsorbent had the highest removal efficiency at pH=2. At high pH levels, the functional groups of hydroxyl at the surface of adsorbents with negative charge cause the repulsion of anionic phosphate, so with the increase of pH, the efficiency of phosphate adsorption by nanoparticles reduces, while at low pH levels, with regard to the negative charge of phosphate ions, the electrostatic attraction between the adsorbent and the pollutant increases, and the efficiency of its adsorption increases too.



**Diagram 3:** The removal efficiency of phosphate and adsorption capacity of nanoparticle against pH changes using PAC-MNPs adsorbent, in initial phosphate concentration of 1 mg/L, and adsorbent dosage of 1 m, with a g/L contact time of 1 hour and stirring speed of 300 rpm.

**3.2. The effect of adsorbent dosage**

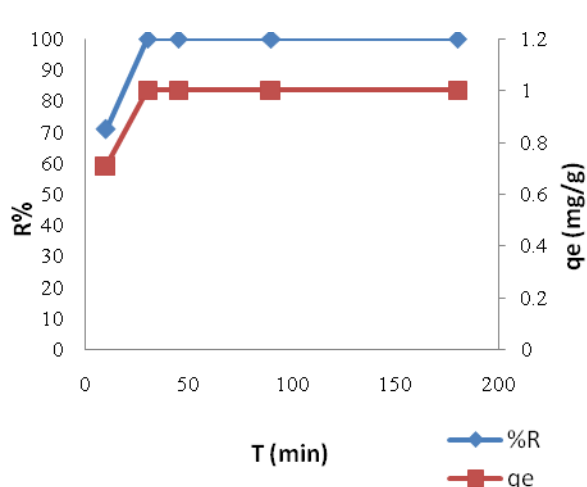
**Diagram 4** shows that the increase of adsorbent dosage from 0.5 to 1 g/L, the removal percentage increased, but higher doses had little effect on the removal rate of phosphate by nanoparticles. Therefore, in the next stages, for PAC-MNPs an amount of 1 mg/L was optimally chosen and used.



**Diagram 4:** The removal efficiency of phosphate and adsorption capacity of nanoparticle against adsorbent dosage changes using PAC-MNPs adsorbent, in initial phosphate concentration of 1 mg/L, pH=2, with a contact time of 1 hour and stirring speed of 300 rpm.

**3.3. Examining the effect of contact time**

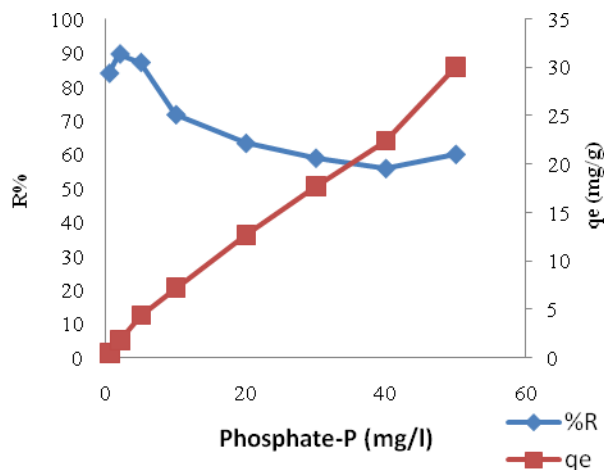
with contact time increases the removal efficiency increases. Because with increase in time, the possibility of accessibility of adsorption active sites increases. And the optimal contact time for adsorbent was obtained to be 90 minutes, the results of which are shown in the **Diagram 5**.



**Diagram 5:** The removal efficiency of phosphate and adsorption capacity of nanoparticle against contact time changes using PAC-MNPs adsorbent, with dosage of 1 g/L, in initial phosphate concentration of 1 mg/L, pH=2, and stirring speed of 300 rpm.

**3.4. Examining the effect of changes in initial concentration of phosphate**

As initial concentration of phosphate increases the removal efficiency decreases and adsorption capacity increases, which is due to the filling of active sites of nanoparticles adsorption, which with increasing the phosphate concentration, desorption process of nanoparticles occurs gradually. **Diagram 6** shows the effect of initial concentration changes of phosphate



**Diagram 6:** The removal efficiency of phosphate with changes of initial phosphate concentration by using PAC-MNPs adsorbent, with dosage of 1 g/L, pH=2, with contact time of 30 minutes and stirring speed of 300 rpm.

**3.5. The effect of interferences**

Since the possibility of interference is considered as a defect, in this study the effect of interference of other ions

on the removal of phosphate was tested. Interference effects of ions were investigated in the same phosphate concentration level, and in 10 and 100 times more concentrated than that of phosphate.

### 3.6. Examining the adsorption isotherms

The results from the isotherm of Langmuir and Freundlich's adsorption model and the related coefficients are presented in [table 1](#). Based on the results, the present study was more in matching with Freundlich adsorption equation.

**Table 1:** The results of isotherms study

Langmuir's isotherm			Freundlich's isotherm		
qm (mg/g)	KL(L/mg)	R2	Log Kf	n	R2
0.0366	5.977	0.832	0.571	1.503	0.958

## 4. Discussion

According to a study by Yanzhong Li et al (2014), the highest phosphate removal was at pH=7, but in the present study a better removal efficiency occurred at pH=2, which was due to the difference in the structure of nanoparticles (16). Also in Jiao Yang et al (2011), the amount of phosphate adsorption in water by La-EDTA-Fe<sub>3</sub>O<sub>4</sub> 97.8% was 7 hours. This process follows the Langmuir isotherm and it was found that the highest amount of adsorption was obtained at pH=6-7, but in the present study, the percentage of removal for the magnetic powder activated carbon adsorbent was 100% at pH=2. In the present study, low pH levels with regard to the negatively charged phosphate ions, the electrostatic attraction between the adsorbent and the pollutant increases and its adsorbing efficiency increases too (3).

Figure 8 shows the effect of initial concentration changes of phosphate. Rafati et al (2012) showed that with the increase in phosphate concentrations, the resin adsorption capacity increased (10). In this study phosphate removal efficiency decreased with increasing concentration; and in the present study with the increase in phosphate concentration the removal efficiency decreased, which is due to the saturation of adsorption sites. As initial concentration of phosphate increases the removal efficiency decreases and adsorption capacity increases, which is due to the filling of active sites of nanoparticles adsorption, which with increasing the phosphate concentration, desorption process of nanoparticles occurs gradually.

Rafati et al, (2011) showed that with the increase in phosphate concentration, the adsorption capacity of resin

increased. Also, the chloride ions, sulfate, bicarbonate and the total of above anions had no effect on the performance of resin in phosphate removal, but in the case of powdered activated carbon sorbent coated with magnetic nanoparticles of iron for the phosphate removal it was found that with increasing the concentration of phosphate the removal efficiency was reduced, which was due to the saturation of adsorption sites. Also, by increasing the concentration of magnesium cations and sulfate anions, the removal efficiency is somewhat reduced, while changes in the concentration of calcium cations and carbonate and chloride anions had little impact on removal efficiency of these nanoparticles in the removal of phosphate. Therefore, the resulting nanoparticles will have high efficacy in real samples (10).

The study by Amin et al (2014), in examination of powdered activated carbon performance (PAC) on the removal of natural organic material (NOM) from drinking water, showed that the results were consistent with Freundlich's adsorption isotherm, which was in line with the present study (17). Also, based on the study by Joneidi-Jafari et al (2013), the adsorption of the aniline ACMNPs - Fe<sub>3</sub>O<sub>4</sub> follow Langmuir's isotherm model and the pseudo-second-order kinetic model. Due to advantages such as simple and fast solution separation, synthesized adsorbent (magnetic activated carbon) in both studies can be useful as an effective sorbent to remove contaminants from the water and sewage (18).

## 5. Conclusion

In the present study, based on the examination of the efficacy of synthesized nanoparticles for the removal of phosphate from aqueous solutions, the following points can be concluded: The amount of phosphate adsorption is dependent on the pH of aquatic environment and in pH=2, the greatest adsorption was observed.

- The amount of adsorbed phosphate increased with the increase of phosphate initial concentration.
- In examining the effect of interfering ions, with increasing the concentration of magnesium cations and sulfate anions, the removal efficiency decreased slightly and the concentration of calcium cations and carbonate anions and chloride anions had little impact on the removal efficiency.
- Freundlich isotherm describes the phosphate adsorption model well.



## 6. Acknowledgements

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