

Use of Iron Oxide/Activated Carbon Magnetic Composite for Adsorptive Removal of Arsenic from Water

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Abstract

Activated carbon (AC) and iron oxide are widely used for the arsenic removal from water. In this study, the potential of Fe_3O_4 / Commercial activated carbon composite (Fe_3O_4 / CAC composite) for adsorptive removal of arsenic from water is presented. Fe_2O_3 / Commercial AC composite (adsorbent) was prepared by a one step hydrothermal treatment of aqueous solution containing commercial activated carbon, iron(II)chloridetetrahydrate, polyvinylpyrrolidone (PVP) and ethanol. Batch experiments were conducted to study the adsorption behavior of arsenide onto the magnetic composite adsorbent. The percentage of Arsenic removal by the composite adsorbent was much higher as compared to the plain CAC. The highest percentage of fluoride removal was found at pH 8, adsorbent dose of 1 gm/L and contact time of 70 min. The applicability of the Langmuir and Freundlich models for the arsenide adsorption data was tested. Langmuir model describe the experimental data. The maximum adsorption capacity of the composite adsorbent for Arsenic removal was 7.5 mg/gm. The results of this study show that, Fe_3O_4 / CAC composite can be potentially applied for the treatment of water contaminated by Arsenic.

Keywords: Fe_3O_4 / Commercial activated carbon composite; Adsorption; Arsenic removal; Water.

1. INTRODUCTION

Arsenic is a toxic compound, known for its carcinogenic effects to humans who are chronically exposed to high concentration. Arsenic contamination of waters globally is of major concern, because million of people worldwide are exposed to elevated concentrations in their drinking water¹. Specifically, In Southeast Asia, more than 500 million people consume water with concentrations higher than WHO guideline value of 10 μ g/L (WHO, 2008).

In Nepal, Arsenic (As) contamination is a major issue of current drinking water supply system using groundwater and has recently been one of the major environmental health management issues especially in the Terai (plain) region, where the population density is very high. About 47% of the total population of Nepal lives in Terai (low land) region and 90% of them depends on groundwater as their primary source of drinking water¹. Arsenic contamination in groundwater of the Terai region was first identified by Department of Water Supply and Sewerage (DWSS) and the World Health Organization (WHO) in 1999. Presence of elevated arsenic concentrations (> 6.7 M) in alluvial aquifers within the Terai region is confirmed by recent studies. The

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groundwater of 20 districts of this region (Sunsari, Saptari, Siraha, Dhanusha, Sarlahi, Rautahat, Bara, Nawalparasi, Rupandehi, Kapilbastu, Banke, Kailali, Kanchanour etc.) has been found to be contaminated with high concentration of Arsenic². It is estimated that, half a million people inhabiting this region are believed to have been exposed to arsenic levels greater than 50 μ g/L. Thirty-one percent of the population (3.5 million) have been exposed to arsenic levels between 10 and 50 μ g/L³.

Arsenic occurs in the aqueous system in several oxidation states (-3, 0, +3, +5). In natural water, inorganic arsenic is mostly found as trivalent arsenide or prevalent arsenate. The trivalent arsenic (Arsenide, As (III)) is more mobile and toxic (40-60 times) than the pentavalent arsenic (Arsenate, As (V)). In surface water under oxidizing conditions, arsenate predominates while in anoxic water under reducing conditions, arsenide becomes stable. At near neutral pH, the predominant species are H_2AsO_4^- and $\text{H}_2\text{AsO}_2^{4-}$ for arsenate, and unchanged H_3AsO_3 for arsenide. Inorganic species of arsenic (AS (III) and As (V)) represent a potential threat to the environment, human health, and animal health due to their carcinogenic and other effects. Permanent arsenic intake can lead to chronic intoxication, and prolonged arsenic exposure can damage the central nervous system, liver, and skin and results in the appearance of diverse types of cancers, such as hyperkeratosis, lung, skin, and prostate cancers⁵. Therefore, the removal of arsenic from drinking water is of critical importance.

Several methods have been applied over the years on the removal of arsenic present in water and wastewater. These are chemical precipitations, conventional coagulation, reverse osmosis, ion exchange and adsorption or sorption. One of which, adsorption method, is simple and cost-effective, thus has been widely used. Among various adsorbents, adsorption onto activated carbon has proven to be one of the most effective and reliable physiochemical treatment methodologies. Due to its high surface area and porous structure it can efficiently adsorb gases and compounds dispersed or dissolved in liquids.

The application of magnetic particle technology is one of the choices for field application of the activated carbon adsorbent. Adsorption of arsenic using magnetic carbon nano composite for removal of arsenic contamination from water is reported by many researchers in the last decades (Lin and Chen, 2014). In order to introduce magnetic properties of nano composites, various metallic materials have been utilized including iron, nickel and cobalt. Most studies have considered iron-based magnetic material due to their higher magnetic character and lower cost⁶. The most frequently used magnetic particle is iron oxide, especially magnetite and maghemite⁷. Fe (III) has high affinity for inorganic As species and selectively performs As sorption. Inner sphere surface complexation can explain the strong interaction between As (V) and various Fe oxides. Especially, hydrous ferric oxide is most effective for removing both As (III) and As (V) from aqueous solution because of its high specific surface area and iso-electric point.

In this study, a commercially available activated carbon with high efficiency for organics removal has been chosen. It was modified by composting with iron oxide precursors by hydrothermal method. To our Knowledge, the preparation of magnetic composites based on activated carbon and iron oxide and their adsorption properties for arsenic have few been reported so far. Under such circumstances, our aim was to study the potential of $\text{Fe}_3\text{O}_4/\text{CAC}$ magnetic composite for adsorptive removal of arsenic from water.

2. EXPERIMENTAL

2.1 Material

All the chemicals used in the study were of analytical grade. Commercial activated carbon (Fischer Scientific) was used for preparation of magnetic composite. Iron (II) chloridetetrahydrated ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) (Samchun Chemicals), Liquor Ammonia (NH_3) (Fischer Scientific) and Polyvinylpyrrolidone (PVP, MW-

5800) (Alfa Aesar) were used. All the solutions in this study were prepared using distilled water.

2.2 Preparation of Fe/AC composite

For the preparation of magnetic activated carbon composite for arsenic removal, a one step hydrothermal approach was followed. The sample was prepared by dissolving 400 mg FeCl₂.4H₂O and 10mg of PVP in 20 ml of distilled water. Then 1 ml of ammonia solution was added with constant stirring for 45 minutes using magnetic stirrer. A suspension of 50 mg AC in 10 ml of distilled water and 5 ml of ethanol was added to the former solution. The mixture was then transferred to autoclave for hydrothermal treatment at 130°C for 3 hours. After cooling at room temperature, the obtained product was filtered and washed repeatedly with distilled water and ethanol and was dried in oven at 30°C for 12 hours and at 80°C for 6 hours. The resultant composite was finally stored in polystyrene bottles for further usage.

2.3 Adsorption experiments

Adsorption experiments were performed by batch method. A definite amount of Fe₃O₄/CAC composite was suspended in 25 mL of Arsenic solution in 100mL plastic conical flasks. The suspension was agitated on VDRL shaker at 160rpm at room temperature. After equilibrium, the suspension was filtered and Arsenic concentration in the filtrates was analyzed for the residual concentration of Arsenic by the molybdenum blue method using Spectrophotometer at 840nm.

The effect of adsorbent dose on percentage of Arsenic removal by composite adsorbent was studied by varying the adsorbent dose from 1gm/L to 2 gm/L. During study, other parameters kept constant such as the initial Arsenic concentration 5mg/L, contact time 1 hr. Effect of pH on the percentage of Arsenic removal by the composite adsorbent was studied in the pH range of 2 to 10 keeping other parameters constant such as adsorbent dose 1gm/L, initial Arsenic concentration 5 mg/L and contact time 1 hrs. pH of the solution was adjusted by adding 0.1N HCL and 0.1N NaOH. The effect of contact time on the percentage of Arsenic removal by composite adsorbent was studied at different contact time from 5 min to 300 min by keeping other parameters constant such as the adsorbent dose 1gm/L, initial Arsenic concentration 5 mg/L. All the experiments were carried out at room temperature. The percentage removal of As was calculated by using the following equations (1).

$$\text{Removal percentage} = \frac{(C_0 - C_e) \times 100}{C_0} \quad (1)$$

Where C₀= Initial concentration of Arsenic (mg/L),

C_e= equilibrium concentration of Arsenic (mg/L)

2.4 Adsorption isotherms study

Adsorption isotherms study was conducted with arsenic solutions of different initial concentrations from 2 mg/L to 120 mg/L. The other parameters were kept constant such as adsorbent dose 1gm/L, and contact time 1hrs during the experiment. The milligram of Arsenic per gram of adsorbent, q_e (mg/gm) adsorbed was calculated by using the following equation.

$$q_e(\text{mg/gm}) = \frac{(C_o - C_e) \times V}{M} \quad (2)$$

Where, V = volume of As (III) solution (L) and M = mass of the adsorbent (gm).

3. RESULT AND DISCUSSION

3.1 Adsorption studies

Comparison on percentage of removal of CAC and composite adsorbent were carried out. The percentage of arsenic removal by CAC and composite adsorbent is presented in Figure 1.

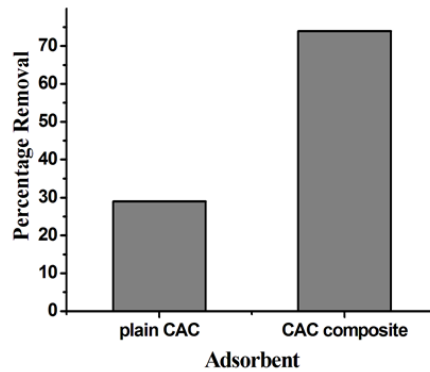


Figure 1. Percentage of arsenic removal by $\text{Fe}_2\text{O}_3/\text{CAC}$ composite and CAC

The percentage of arsenic removal by CAC is found to be less than 29 %, but the adsorption capacity increased to 74 % by using the composite adsorbent. It clearly indicates the synergistic effect of AC for adsorption of arsenic. Thus, the composite of CAC is much better adsorbent than individual components for arsenic removal.

3.2 Effect of pH

pH of the solution is an important parameter in arsenic adsorption, since it affects the surface charge of the adsorbent. Figure 2 represents the effect of pH on the percentage of arsenic removal by the composite adsorbent.

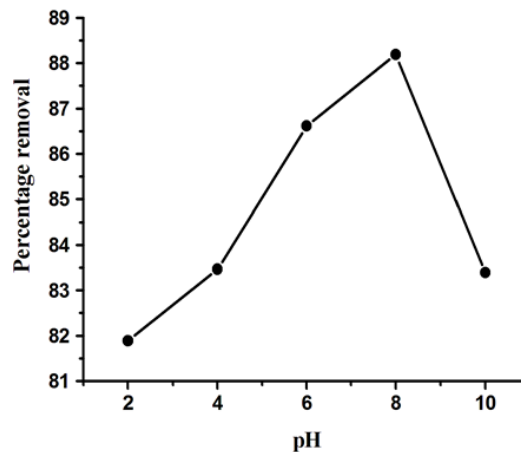


Figure 2. Effect of pH on the percentage removal

As shown in the Figure-2, it can be noticed that the maximum adsorption capacities of composites adsorbent for As (III) occurred at pH 6.0-9.0. The highest removal efficiency has taken place at pH 8.0 (88.18%). It was found to that the adsorption of As(III) was lower at lower pH, attained maximum value at pH 8 and further decrease with increase in pH. The As (III) below the pH 8 exists principally as H_3AsO_3 . The predominant monomeric (H_3AsO_3) and neutral (H_3AsO_3) species are thus considered to be responsible for adsorption of As (III) by substitution of the hydroxyl ions or water molecules at pH 8. In addition when pH increases, there is decrease in positive surface charge because of the deprotonation of the adsorbent functional groups which results in lower electrostatic repulsion between the H_3AsO_3 and the hydroxyl ion. Therefore charges on the surface of composite become negative with the increase in pH and leading to increase in attractive forces between H_3AsO_3 and hydroxyl ion. It results in the enhancement of adsorption of As (III) and maximum adsorption of As (III) from solution.

3.3 Effect of pH

The effect of adsorbent dose on the percentage removal is shown in Figure 3. The percentage removal of arsenic increases rapidly with an increase in adsorbent dose, but beyond a dose of 20 mg/L, further addition of the composite adsorbent did not change percentage removal. The removal of As (III) increases from 59.45 to 95.32% with increase in adsorbent dose from 1.0 gm/L to 2.0 gm/L. This can be explained as increase in adsorbent dosage increases the availability of large surface area and more adsorption sites. At low adsorbent dose, the adsorbent surface becomes saturated with As (III) and the residual As (III) ion concentration in the solution is large enough^{11, 12}. Thus 1.0 gm/L composite adsorbent was chosen for further study.

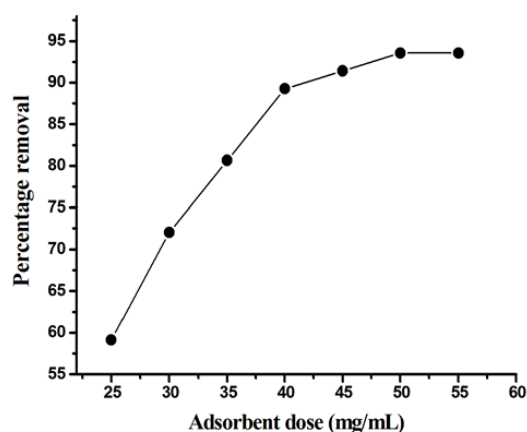


Figure 3. Effect of adsorbent dose on the adsorption of As(III)

3.4 Effect of contact time

The effect of contact time on the adsorption of 5mg/L As(III) with 25 mg of adsorbent is shown in Figure 4. As it is shown, the removal efficiency of As(III) onto the composite adsorbent significantly increase during the initial adsorption stage (0-70 min) and then continue to increase at a relatively slow speed with contact time until a state of equilibrium is reached after 70 min. There was no significant change in As(III) removal

rates after 60 min to 400 min. Based on the results 1h was taken as the time in adsorption experiments.

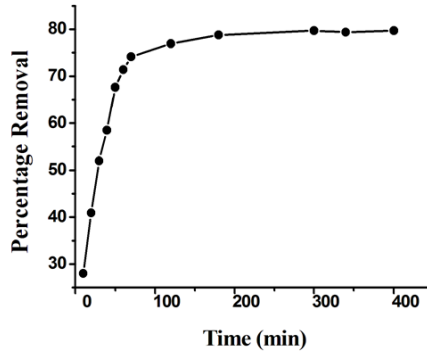


Figure 4. Effect of contact time on the adsorption of As(III)

The adsorption rate was rapid at first because of the presence of large number of sites so that large amount of As(III) ions get attached selectively to the adsorbents sites initially. The rate slowed down gradually till it attained equilibrium at specific time beyond which there was no significant increase in adsorption rate due to decrease in active sorption sites in the adsorbent and after the saturation point adsorption becomes constant.

3.5 Adsorption Isotherm

The main objectives of adsorption isotherm is to study the capacity of the modified activated carbon adsorbent to sequester As(III) from an aqueous solution. This study was analyzed by using Langmuir and Freundlich models.

Langmuir isotherm: The Langmuir equation applied for adsorption equilibrium is as follows:

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m}$$

Where C_e = equilibrium concentration (mg/L)

Q_e = amount adsorbed under equilibrium (mg/L)

Q_m = theoretical maximum adsorption capacity corresponding to complete monolayer coverage (mg/gm)

b = Langmuir constant, q_m and b are determined from the slope and intercept from Langmuir model. The Langmuir model assumes that the adsorption of the metal ions occurs on a homogeneous surface by monolayer without any interaction between the adsorbate and adsorbent.

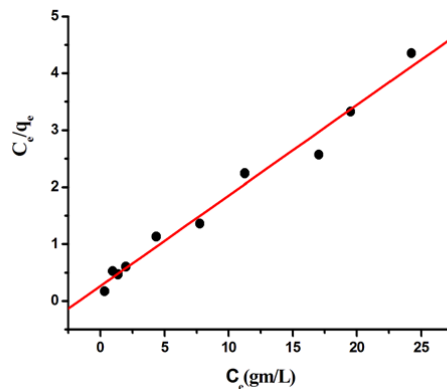


Figure 5. Langmuir Adsorption isotherm for the adsorption of As(III) onto composite

3.6 Freundlich isotherm

It can be expressed in the linear form as follows:-

$$\log q_e = \log K + \frac{1}{n} \log C_e$$

Where K= Freundlich constant and n = adsorption intensity

It assumes that the uptakes of metal ions occur on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration.

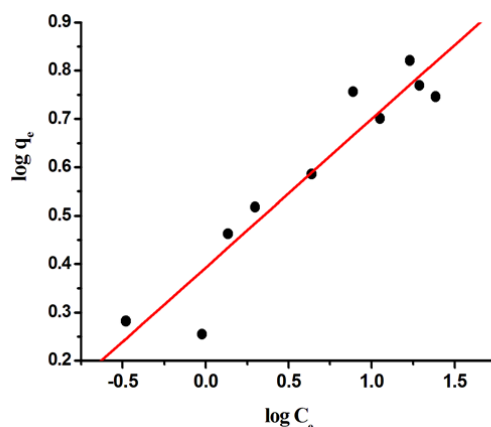


Figure 6. Freundlich adsorption isotherm for the adsorption of As(III) onto composite

Adsorption of As(III) onto the CAC composite gives the linear relationship with Langmuir and Freundlich isotherm which are shown in Fig.5 and Fig.6. Langmuir and Freundlich parameters are determined from the slope and intercept of their respective plots and results obtained are presented in Table 1. The values of Langmuir equilibrium parameter between 0 and 1 indicated that equilibrium data fits well with Langmuir adsorption isotherm. The values of Freundlich parameter between 0 and 1 indicated that adsorption process was favorable. However, the correlation coefficient values for Langmuir isotherm were found to be greater than that of Freundlich isotherm indicating that the adsorption process is better defined by the Langmuir isotherm model than by the Freundlich. It indicates that the distribution of active sites is homogeneous. The monolayer sorption capacity of CAC composite for As(III) was found to be 7.518 mg/gm.

Table 1. Langmuir and Freundlich Parameters for the adsorption of As(III) onto CAC magnetic composite

Species	Adsorbent	Langmuir isotherm			Freundlich isotherm		
		qm(mg/g)	b(L/mg)	R ²	K(mg/g)	1/n	R ²
As(III)	CAC composite	7.518	0.634	0.982	2.671	0.518	0.921

4. CONCLUSION

A magnetic composite adsorbent was successfully prepared with activated carbon and iron oxide as raw materials for the removal of Arsenic from solution. The performances of the composite adsorbent were compared to those of plain activated carbon, the adsorbent showed high adsorption capacities for arsenic. The adsorption properties of the composite adsorbent for Arsenic depend on contact time, initial solution, pH and adsorbent dosage. The equilibrium data obtained from this study was well presented by Langmuir and Freundlich models. It shows monolayer adsorption of Arsenic on composite

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