



Adsorption of nitrate from aqueous solution using activated carbon-supported Fe^0 , $\text{Fe}_2(\text{SO}_4)_3$, and FeSO_4

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Original Article

Abstract

In this laboratory scale study, impregnated almond shell activated carbon was used as adsorbent to investigate its feasibility for nitrate adsorption from aqueous medium. The effects of activated carbon dosage and contact time have been examined in batch experiments. Experimental data show that Fe^0 , $\text{Fe}_2(\text{SO}_4)_3$, and FeSO_4 impregnated activated carbons were more effective than virgin almond activated carbon in nitrate removal. The maximum nitrate removal was 70% and 10-15% for modified activated carbons and virgin activated carbon, respectively. These experiments were conducted at pH 6.2, 20 °C, and initial concentrations of 20 mg/l nitrate-N. The increase in modified activated carbon dosages increased the removal of nitrate. The equilibrium time was found to be 30 min for modified activated carbons.

KEYWORDS: Activated Charcoal, Adsorption, Nitrate Removal, Wastewater

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Introduction

Due to increased anthropogenic activities nitrate contamination of soil has become an environmental and health problem in many countries. The intensive application of nitrogen fertilizers, irrigation with wastewater, and manure application are the most significant causes of nitrate pollution.¹ Increased levels of nitrate can create the potential for eutrophication and toxic algal blooms in the receiving water.² High concentrations of nitrate result in diseases in newborns such as infant cyanosis or blue baby syndrome and cancer.^{3,4} The European Union and the US Environmental Protection Agency determined 5.6 mg ($\text{NO}_3\text{-N}$)/l and 10 mg ($\text{NO}_3\text{-N}$)/l as the standard values of drinking water, respectively.⁵

Several physicochemical and biological processes have been investigated for the removal of nitrate from water and wastewater. Adsorption method is promising, since it is simple and economically efficient. Several adsorbents such as fly ash⁶, agricultural waste⁷, natural clays⁸, and bamboo powder charcoal⁹ have been investigated as adsorbents for the removal of nitrate.

The activated carbon (AC) mainly contains micropore, which is efficient in the removal of some pollutants. In some cases, mesopores are needed to improve adsorption velocity and mass transfer. Therefore, it is necessary to increase the mesopore content of AC. One of the most effective approaches to increasing the mesopore and micropore volume of AC is to catalyze the steam activation reaction of carbon by using

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transition metals or rare earth metal compounds, which can promisingly promote the mesopore formation.¹⁰

The generation mechanism of mesopore and micropore is the activation reaction which takes place in the immediate vicinity of metal particles, leading to the formation of mesopores and micropores by pitting holes into the carbon matrix. The impregnation optimizes the existing properties of the AC, giving a synergism between the chemicals and the carbon.^{11,12} This facilitates the cost-effective removal of certain pollutants which would be impossible otherwise. The unique structure of AC provides a very large surface area. AC has an extraordinarily large surface area and pore volume that gives it a unique adsorption capacity.¹³ Organic molecules and AC are similar materials; therefore, there is a stronger tendency for most organic chemicals to associate with the AC rather than stay dissolved in a dissimilar material like water. Generally, the least soluble organic molecules are most strongly adsorbed. Often the smaller organic molecules are held the tightest, because they fit into the smaller pores.¹⁴

Adsorption usually increases as pH and temperature decrease. Chemical reactions and forms of chemicals are closely related to pH and temperature. When pH and temperature are lowered, many organic chemicals assume more adsorbable forms.¹⁴ AC is not widely used in practice for nitrate control due to the low capacities and slow adsorption kinetics of nitrate by commercially available ACs. In the present work, nitrate removal was carried out by a series of modifications and well characterized almond shell ACs with Fe^0 , $\text{Fe}_2(\text{SO}_4)_3$, and FeSO_4 .

Materials and Methods

Almond activated carbon was stirred in a boiling solution containing Fe^0 , $\text{Fe}_2(\text{SO}_4)_3$, and FeSO_4 (5 wt. % based on AC) at room temperature, and filtered and dried at 120°C. At the end of preparation, modified carbon was extensively washed with

normal perchloric acid and deionized water. After washing, the AC were dried at 90 °C in a drying oven and stored in a desiccator until use. The AC particles between 10 and 20 mesh sizes with 1 mm effective size and 1.18 uniformity coefficients were used in all experiments.

Batch adsorption experiments were conducted in different conical glass flasks in a shaking thermostat with a constant speed of 120 rpm. For each batch adsorption, 50 mL of solution containing 20 mg/l $\text{NO}_3\text{-N}$ concentration of nitrate with desired level of adsorbents (0, 1.5, 3, 4.5, and 6 g AC) and contact time variations (10, 20, 30, 40, 50, 60, 90, and 120 min) were used. All experiments were conducted in triplicate and average values of adsorption are presented in subsequent sections. Potassium nitrate was used as the source of nitrate in all the experiments (Merck, Darmstadt, Germany). The percentage of nitrate removed has been measured calorimetrically using a UV-visible spectrophotometer (Philips PU 8700 Series model). The experiments have been conducted at 20°C for the impregnated AC and AC.

AC was characterized for surface morphology and composition. The surface morphology of the adsorbents was observed using scanning electron microscopy (SEM) technique (XL30-Philips model). The metals on ACs were demonstrated by SEM (Model XL30, Philips, Eindhoven, Netherlands) equipped with energy dispersive x-ray microanalysis (EDX) and analysis system of ZAF software (Model XL30, Philips, Eindhoven, Netherlands).

Nitrate was analyzed using UV-visible spectrophotometer. The concentration of ammonia was measured using the Nesslerization method, as described in the standard methods of water and wastewater examination, and the concentration of nitrite was analyzed by sulphanilamide method at 543 nm. Fe and sulfate were regularly checked for untreated and treated effluents according to the standard methods.¹⁵ AC properties such as apparent and bulk densities, iodine adsorption test, moisture content (%), and particle size were

analyzed according to ASTM D 2854, ASTM D 4607, ASTM D 2867, and ASTM D 2862, respectively.

Results and Discussion

After modification of activated carbons, physicochemical characteristics were determined. Physicochemical characteristics of almond shell AC and impregnated AC are shown in table 1. The results were obtained from the mean of triplicate samples for every variable. Surface morphology and chemical characterization of ACs were estimated by SEM and analysis system of ZAF software, respectively. For preparation of SEM, The ACs were dried in a CO₂ atmosphere under critical conditions. The SEM micrographs of AC and impregnated AC are displayed in figure 1.

The x-ray microanalysis of ACs is demonstrated in figure 2. Fe was not indicated in EDX elemental analysis of no modified AC (AC₀), while Fe increased on the surface of the impregnated ACs (carbon exception). The effects of contact time on the removal of nitrate by AC with the initial concentration of 20 mg/l NO₃-N, 20°C temperature, and pH 6.2 are shown in figures 3 and 4.

Batch adsorption experiments have been carried out by taking various doses of adsorbent (1.5, 3, 4.5, and 6 g ACs/50cc nitrate solution) in different conical glass flasks in a shaking thermostat with a constant speed of 120 rpm. Initial solution pH and temperature were adjusted to 6.2 (using HCl and NaOH) and 20 °C, respectively. The effect of carbon dosages on the adsorption process is shown in figure 5.

Table 1. Physicochemical characteristics of almond activated carbons and activated carbon modifications

Parameters	AC-0	AC-Fe	AC-FeSO ₄	AC-Fe ₂ (SO ₄) ₃
Apparent (bulk) density (g/ml)	0.42	0.38	0.42	0.44
Iodine adsorption test	375.00	222.00	395.00	350.00
Moisture content (%)	3.30	4.79	8.60	8.75
pH	3.72	3.04	2.76	2.65

AC: Activated carbon

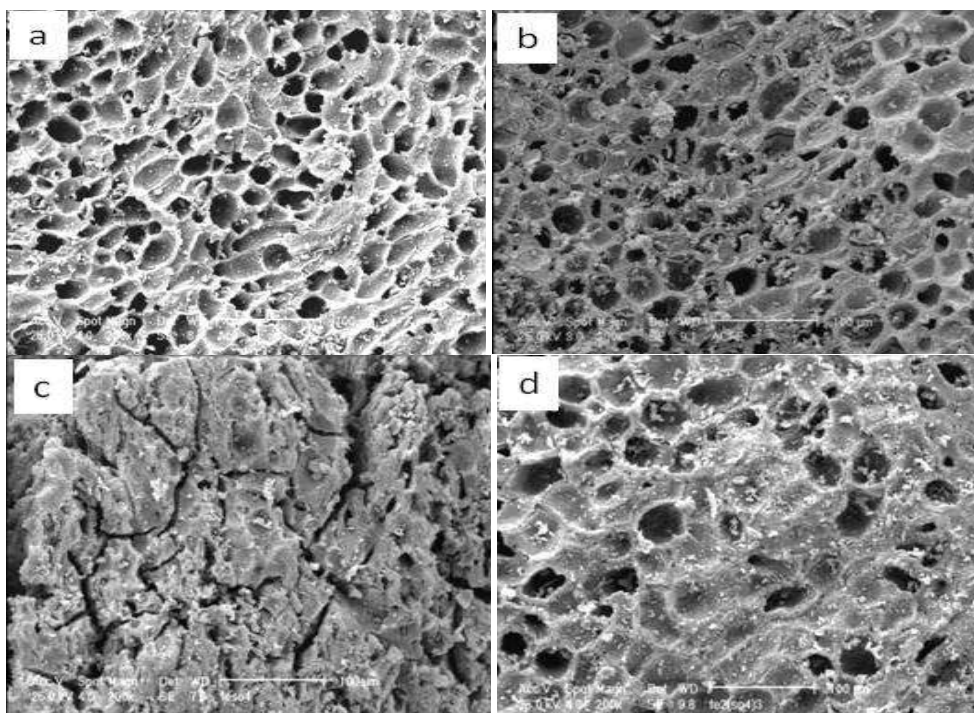
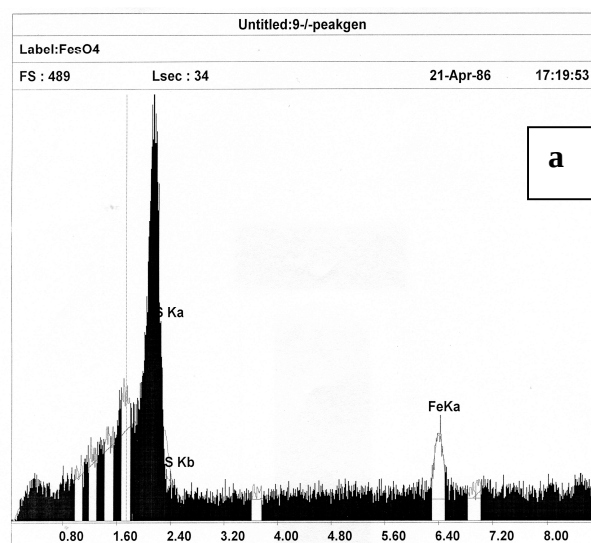
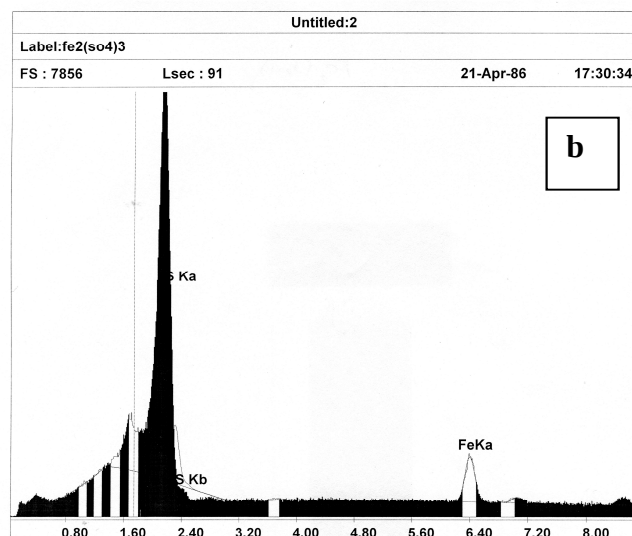


Figure 1. Morphological image of a: AC-0, b: AC-Fe, c: AC-FeSO₄, and d: AC-Fe₂(SO₄)₃
AC: Activated carbon



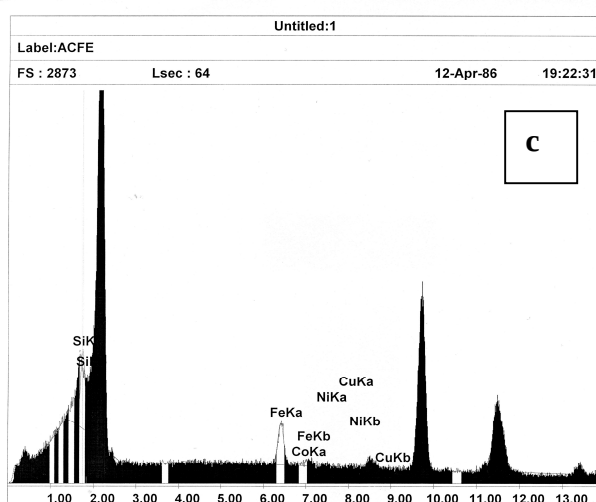
Element	Wt %	At %
S O3	34.69	51.44
Fe2O3	65.31	48.56
Total	100.00	100.00

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
S K	14.56	20.37	6.87	0.71
Fe K	29.74	11.69	3.66	2.54



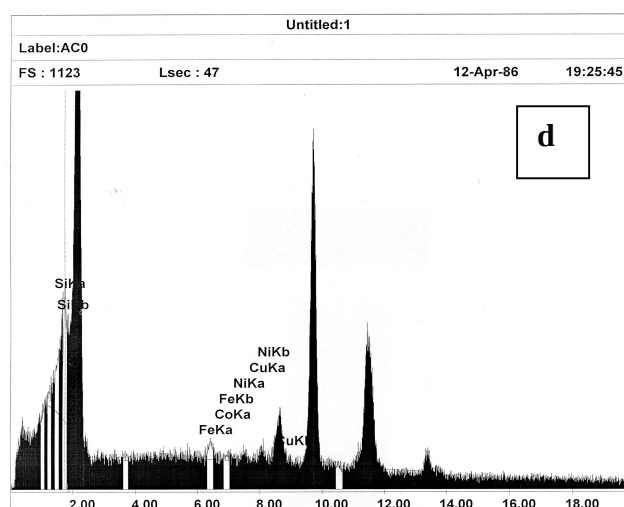
Element	Wt %	At %
S O3	50.26	66.84
Fe2O3	49.74	33.16
Total	100.00	100.00

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
S K	121.02	88.80	1.25	1.36
Fe K	122.37	51.26	1.12	2.39



Element	Wt %	At %
Si K	46.09	63.33
Fe K	42.42	29.32
Co K	2.41	1.58
Ni K	5.25	3.45
Cu K	3.83	2.32
Total	100.00	100.00

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
Si K	91.09	81.36	1.80	1.12
Fe K	64.17	35.39	1.94	1.81
Co K	3.13	33.77	24.22	0.09
Ni K	5.64	33.83	13.91	0.17
Cu K	3.44	33.19	21.94	0.10



Element	Wt %	At %
Si K	55.36	72.54
Fe K	12.05	7.94
Co K	3.85	2.41
Ni K	9.97	6.25
Cu K	18.77	10.87
Total	100.00	100.00

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
Si K	84.04	52.61	2.02	1.60
Fe K	14.32	30.78	6.81	0.47
Co K	3.94	30.06	21.49	0.13
Ni K	8.55	30.95	10.67	0.28
Cu K	13.31	29.87	7.17	0.45

Figure 2. The x-ray microanalysis of activated carbons a: AC-FeSO₄, b: AC-Fe₂(SO₄)₃, c:AC-Fe, and d:AC-0

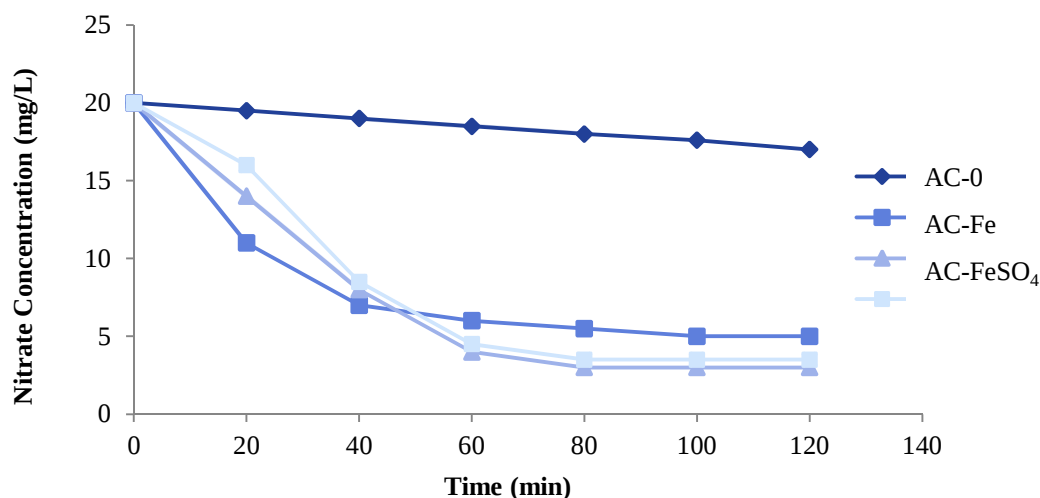


Figure 3. Effect of different activated carbons (AC) on nitrate-N removal ($T = 20^{\circ}\text{C}$, $\text{Co} = 20 \text{ mg/l}$, and $\text{pH} = 6.2$)

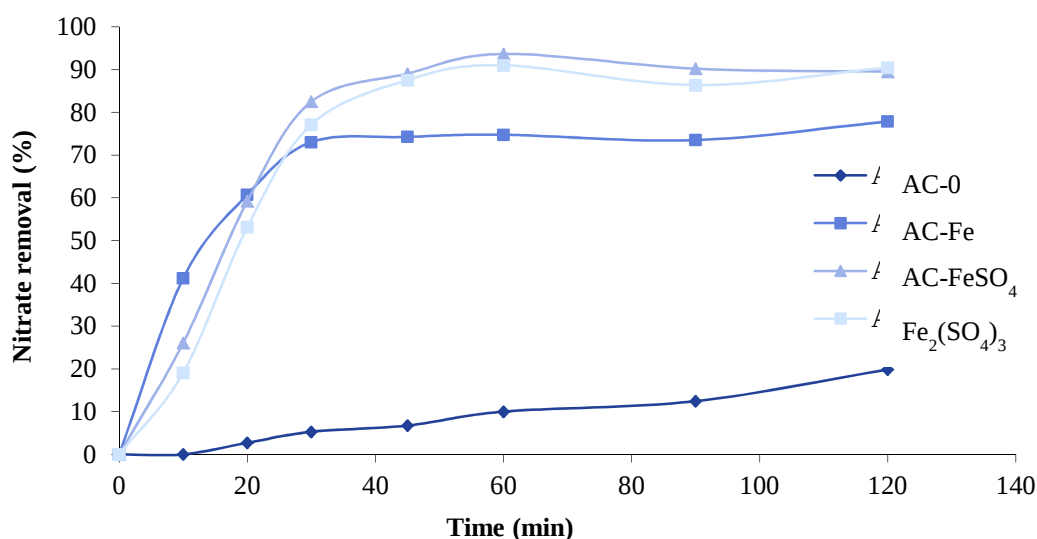


Figure 4. Nitrate removal curve for different activated (AC) carbons ($T = 20^{\circ}\text{C}$, $\text{Co} = 20 \text{ mg/l}$, and $\text{pH} = 6.2$)

To identify the regeneration capacity of the adsorbent, the ACs (AC-0, Fe^0 , $\text{Fe}_2(\text{SO}_4)_3$, and FeSO_4) were agitated with 50 ml of nitrate solution at different concentrations and nitrate isotherms were determined. Nitrate isotherms of all activated carbons in mass basis are shown in figure 6. Water quality after AC treatment is shown in table 2. The water quality was in the range of WHO guideline.

Nitrate could be effectively removed by AC

that was impregnated in the presence of Fe^0 , $\text{Fe}_2(\text{SO}_4)_3$, and FeSO_4 . Bulk density and apparent density increased by modification of almond shell AC (Table 1). The SEM micrographs of ACs (Figure 1) show that original AC (a) became dark after modification (b, c, and d); the surface of modified AC lost its metallic glaze and its color turned black. The comparison of figures a, b, c, and d shows that macropore AC is converted to micropore AC by modification of AC using Fe^0 ,

$\text{Fe}_2(\text{SO}_4)_3$, and FeSO_4 . This phenomenon increased ions adsorption such as nitrate. The SEM micrographs and energy dispersive x-ray microanalysis of ACs (Figure 2) support this fact. It was shown that AC-0 have 0% Fe of total elements (carbon exception) on the surface (Figure 2), while with modification by Fe^0 , $\text{Fe}_2(\text{SO}_4)_3$, and FeSO_4 , Fe increased on the surface of AC-0.

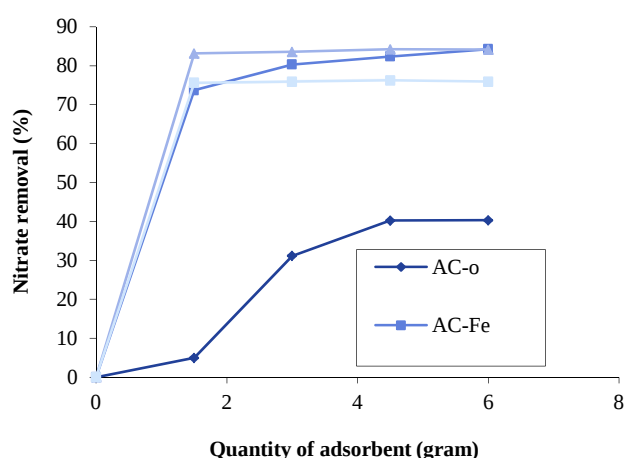


Figure 5. Effect of the quantity of adsorbent activated carbon (AC) and variation in nitrate-N removal percentage with weight of adsorbent on nitrate removal ($T = 20^\circ\text{C}$, $C_0 = 20\text{ mg/l}$, and $\text{pH} = 6.2$)

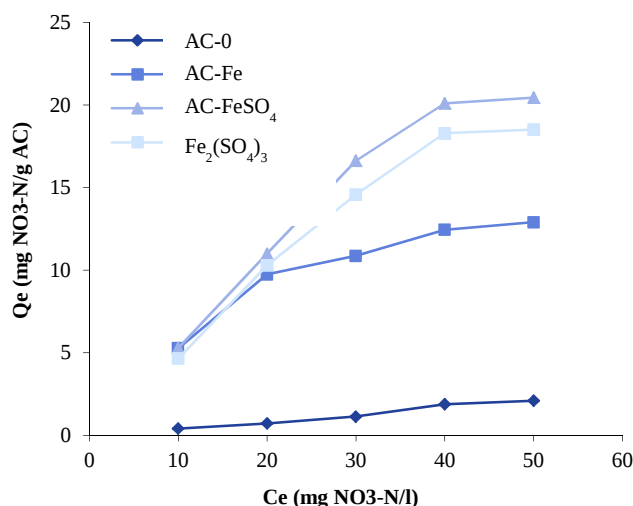


Figure 6. Nitrate-N isotherms of all activated carbon in mass basis

The studies conducted by Shen et al.,¹⁰ and Namasivayam and Sangeetha¹² support this finding. Figures 3 and 4 show the effect of different ACs on nitrate removal from solution with 20 mg/l nitrate-N concentration. When AC₀ is used, 15 mg/l nitrate is removed in 30 minutes reaction. The final nitrate concentration gained was in the standard range of the WHO recommendation for water quality when impregnated ACs is used. It was evident that the modification of AC with Fe^0 , $\text{Fe}_2(\text{SO}_4)_3$, and FeSO_4 greatly enhanced nitrate removal. This phenomenon may be caused by adsorption and chemical reactions. Moreover, AC- FeSO_4 and AC- $\text{Fe}_2(\text{SO}_4)_3$ showed the highest removal capacity for nitrate, which was almost 70-80% in a 30 minute reaction. The equilibrium time for impregnated ACs was found to be 45 minutes. Namasivayam and Sangeetha investigated the removal of anions, heavy metals, organics, and dyes from water by adsorption on to ZnCl_2 activated coir pith carbon.¹² Their findings showed a 95% removal of nitrate by ZnCl_2 coir pith carbon at initial concentration of 20 mg/l, temperature of 35°C , 200 rpm, and agitation time of 3 hour. However, this reduction was insignificant for coir pith carbon without ZnCl_2 modification. The mechanisms of nitrate removal included adsorption and chemical reactions. In the modification process, micropores were formed after impregnation of AC with FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$. The SEM micrographs showed that modified-AC has superior micropore content in comparison to its parent sample (Figure 1). Another other advantage of impregnation by FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ is increasing of AC positive charge. This phenomenon increased adsorption of anions such as nitrate. Previous studies which have conducted the same experiments as those in the present study have confirmed its results.^{10,16}

Mizuta et al. studied the removal of nitrate from drinking water using bamboo powder charcoal.⁹

Table 2. Water quality after activated carbon treatment

Adsorbent	pH	nitrite (mg/l)	Ammonia (mg/l)	Sulfate (mg/l)	Fe (µg/l)
AC-0	6.71	0.0175	0.68	0	0
AC-Fe	6.65	0	0.65	0	750
AC-FeSO ₄	5.40	0.0180	0.57	0	1100
AC-Fe(SO ₄) ₃	5.45	0	0.45	0	337

AC: Activated carbon

Adsorption isotherm of nitrate-nitrogen on to commercial AC at 10°C has shown that maximum amount of nitrate adsorption is 1.17 and 0.93 for bamboo powder charcoal and AC, respectively. Shen et al. studied the effect of AC fiber structure and loaded metals on the adsorption of dichloroethylene.¹⁰ In their work, AC was modified and impregnated with copper, which was converted to metal oxides and reduced to elemental substance, and the adsorption properties of dichloroethylene on AC fiber was investigated. The results showed that both the pore structure of AC fiber and metal/oxide loading affected the adsorption capacity of dichloroethylene.

The amount of AC adsorption increased with the increase in carbon dosage and reached a maximum value after a particular dose. The effect of the quantity of adsorbent AC and variation in nitrate removal percentage with weight of adsorbent on nitrate removal is shown in figure 5. Another study which had conducted the same experiments as those in the present study have showed that an increase in adsorbent dosage increased the percentage of nitrate removal and it reached a maximum value after a particular dose.¹⁷ This was in agreement with the results of the present study. Nitrate isotherms of all AC in mass basis are shown in figure 6. Ozturk and Bektas studied nitrate removal from aqueous solution by adsorption on to various materials.¹⁷ The equilibrium time was found to be 45 minutes for AC. Maximum amount of removal in time was 4 mg NO₃ per gram of AC. However, in this paper, maximum removal is over 14 and 15 mg nitrate-N per 1 gram AC for AC-Fe₂(SO₄)₃ and AC-FeSO₄, respectively.

Water quality after activated carbon

treatment is shown in table 2. As illustrated in table 2, all parameter were within the acceptable range recommended by WHO guideline. However, pH modification is needed.

Conclusion

In the present study, impregnated almond shell activated carbon by Fe, Fe₂(SO₄)₃, and FeSO₄, were used as adsorbent to remove nitrate from water. Nitrate concentrations, activated carbon dosage, and time of contact between modified activated carbon and nitrate solution were studied. The mechanisms of nitrate removal included adsorption and chemical reactions. Impregnated activated carbons by Fe⁰, Fe₂(SO₄)₃, and FeSO₄ were more effective in nitrate removal than virgin almond activated carbon. The maximum nitrate removal was 70% and 10-15% for modified activated carbons and virgin activated carbon, respectively.

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

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