INTRODUCTION

Nitrate is found in most of the natural waters at moderate concentrations but is often enriched to the contaminant levels in the groundwater resources mainly from the excessive use of fertilizers and uncontrolled on land discharges of raw and treated wastewater\[9\]. This leads to an increasingly important problem, limiting the direct use of the groundwater resources for human consumption in several...
Nitrate removal by FeCl₃

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parts of the world. The nitrate ion has also been identified as a potential health hazard to infants and pregnant women[13]. This is due to the potential reduction of nitrate to nitrite ion, in the stomach of infants, which can bind with the haemoglobin of the affected babies, thus diminishing the transfer of oxygen to the body’s cells resulting in a bluish skin color often called methaemoglobinemia or the blue baby syndrome[13]. The abundant use of nitrogen fertilizers and contaminated water can lead to excessive nitrate levels in green vegetables. Under certain conditions, nitrate can be converted to much more poisonous nitrite and ultimately even to a carcinogenic nitrosamine which primarily affects the gastrointestinal tract[18].

To protect consumers from the adverse effects associated with the high nitrate intake, the world health organization (WHO) has set standards to regulate the nitrate concentration in drinking water. The drinking water standard set by the WHO for nitrate is 50 mg/l[20]. The conventional processes (coagulation, filtration, chlorination, UV, ozone treatment) applied for water treatment are not useful for the elimination of nitrate ion from the water[13]. Therefore, other methods have to be applied. Several methods that serve to reduce nitrate in drinking water have been presented[13]. Current technologies for removal of nitrate like ion exchange, reverse osmosis are neither selective to nitrate, generate secondary brine wastes and require frequent media regeneration and biological denitrification requires intensive temperature control, constant supply of organic carbon with possibilities of contamination from microorganisms[8]. The use of biological reactor seems to be the most promising technique in the treatment of high nitrate concentration[19]. However, maintaining biological processes at their optimum conditions is difficult, and the problems of contamination by dead bacteria have to be solved to make such processes safety enough to utilize in drinking water treatment. On the other hand, adsorption is a very feasible process for in situ treatment of underground and surface water, due to its cost benefit of application[10]. AC is useful in drinking water treatment because it acts as an adsorbent, and can effectively remove particles and organics from water. Carbon is a substance that has a long history of being used to absorption impurities and is the most powerful absorbent known to man[8]. AC can be produced from a number of agricultural commodities. Among these are hardwoods, grain hulls, almond, corn cobs, and nut shells[19]. AC is carbon which has a slight electro-positive charge added to it, making it even more attractive to chemicals and impurities. Loose granular AC is used extensively in most of the commonly encountered water filters today. The efficiency of the adsorption process is influenced by the characteristics of the carbon (particle and pore size, surface area, density and hardness) and the characteristics of the contaminant (concentration, tendency of chemical to leave the water, solubility of the contaminant and contaminant attraction to the carbon surface)[6].

The medium for an AC is typically petroleum coke, bituminous coal, lignite, wood products, coconut shell or peanut shells, which are all sources of carbon. It is ‘activated’ by subjecting it to steam and high temperature without oxygen. In some cases the carbon may also be processed by an acid wash or coated with a compound to enhance the removal of specific contaminants. This activation produces carbon with many small pores and therefore a very high surface area. It is then crushed to produce a granular or pulverized carbon product. This creates small particles with more outside surface area available for compounds to enter the AC, which results in greater contaminant removal. The source of the carbon and the activation method determine the effectiveness of removal for specific contaminants[14]. AC adsorption is one of the recommended technologies for nitrate removal from water[10]. However, it is not widely used in practice for nitrate control due to low capacities and slow adsorption kinetics of nitrate by commercially available ACs. In the present study, adsorption studies are carried out for treatment of water for nitrate removal by FeCl₃ supported almond shell AC from aqueous.

EXPERIMENTAL

Adsorbents

Almond shell AC was obtained from ‘Kimia Carbon Arak company’, Iran. AC properties such as apparent (Bulk) density, iodine adsorption test, pH and
moisture content analyzed according to ASTMs protocols. In order to increase the mesopore volume and content, the AC was pretreated with the following procedure:\[16\]: immersed in a 5% FeCl\textsubscript{3} solution for 4 h in room temperature, washed with distilled water, dried at 120°C for 2h and stored in a desiccators until use. AC particles (10 - 20 mesh sizes) were used in all experiments. Finally, the modified AC was characterized and stored until it was used in the adsorption tests. Surface morphology of AC was studied by scanning microscopy (XL30 Philips model).

**Batch experiment procedures**

Present study was carried out in batch mode in open system. Potassium nitrate (KNO\textsubscript{3}) was used as the source of nitrate in all the experiments and was manufactured by Merck. Double distilled water prepared in the laboratory were used for preparation of all reagents and all experimental work. Batch adsorption experiments for reduction of nitrate have been carried out by taking various doses of adsorbent, various concentrations and contact time variations with nitrate solution of known initial concentrations in different conical glass flasks at a shaking thermost at with a constant speed of 150rpm. The experiments were conducted in 1L flask with total volume of 500 ml solution in a water bath, which maintains the reaction temperature at 25°C. Initial solution pH was adjusted to desired value by HCl. FeCl\textsubscript{3} was obtained from Merck. Predetermined quantities of FeCl\textsubscript{3}-AC were added in nitrate containing simulated water and mixing was achieved by a mechanical paddle stirrer at 200rpm. Temperature was measured using temperature probe attached with pH meter during the reaction. Liquid samples was pipetted out from the beaker at regular interval of time and collected in specimen tube. FeCl\textsubscript{3}-AC was separated by settling samples for 10 min and decanting the supernatant, which was used for chemical analysis. All experiments were conducted in duplicate and average values are presented in subsequent section.

**Adsorbent dosage studies**

Adsorption of KNO\textsubscript{3} solution by different adsorbent doses (0.25-1.0g) for each adsorbent was carried out at the optimum pH.

**pH studies**

In order to investigate the effects of pH on nitrate adsorption, the pH of the KNO\textsubscript{3} solutions were adjusted to different values (2, 5.5, 7, and 10) by dilute NaOH or HCl solutions. pH adjusted solution and 0.5g adsorbent were used in batch experiments conducted at the determined equilibrium time. The pH value providing the maximum nitrate removal was determined.

**Kinetic studies**

In kinetic studies 50ml KNO\textsubscript{3} solutions and 0.5g adsorbent were used. Batch experiment was repeated at different periods for all adsorbents. Nitrate concentrations in supernatant have been constant after a time period. The period was accepted as equilibrium time for relevant adsorbent.

**Analytic methods**

Aqueous samples were collected by glass syringes at timed intervals, filtered through 0.22μm membrane filters and then analyzed within 24h. Nitrate, ammonia and iron were analyzed by method according to Standard methods for the examination of water and wastewater\[21\]. pH value was measured with digital pH meter (Hach, model Sens Ion 387). The amounts of FeCl\textsubscript{3} on AC were demonstrated by SEM equipped by edx (Energy dispersive x-ray microanalysis) and analysis system of ZAF software. Porous properties was determined using mercury porosimeter (Pascal 440).

**RESULTS AND DISCUSSION**

The use of ACs to remove organic and inorganic pollutants from waters is widely extended, because of their high surface area, micro porous character and the chemical nature of their surface\[18\]. The removal efficiency is influenced by various factors, such as solution concentration, solution pH and ionic strength, and adsorbent modification procedure. However it is not widely used in practice for nitrate control due to low capacities and slow adsorption kinetics of nitrate by commercially available ACs. The evaluation of the AC and FeCl\textsubscript{3}-AC for nitrate removal revealed that: modification of AC with FeCl\textsubscript{3}...
significantly increases its capacity for nitrate removal (Figure 1).

Numerous attempts have been made to correlate the adsorption capacity of ACs with their surface areas and pore structures. Also, the adsorption properties of ACs may be correlated with the chemical nature of the carbon surface rather than with the surface area and the porosity of the carbon. Moreno-Castilla et al. claimed that modification of AC with HCl, HF or HNO₃, apart from removal of the mineral matter, introduced oxygen surface complexes that change the surface chemistry and can alter the surface area and porosity of the original samples[11]. Mostafa (1997) studied adsorption of mercury, lead and cadmium on AC modified with sulphuric acid and observed a significant increase in metal ion adsorption[12]. He proposed that sulphuric acid might introduce acidic surface oxides on the carbon surface. Toles et al. (1999) reported that air oxidation of phosphoric acid ACs yielded carbons with greater copper uptake[17]. Copper adsorption showed good correlation with surface functional groups. Modification of the surface chemistry of ACs might be a viable attractive route toward novel applications of these materials[4].

Figure 1 illustrates the nitrate removal from the solution by AC and FeCl₃-AC. The FeCl₃-AC showed higher adsorption capacity for nitrate removal. The concentration of nitrate were reached to 76 mg/l and 8 mg/l after treating with AC and FeCl₃-AC, respectively. Kinetic study showed that the modifications greatly decreased the adsorption equilibrium time. The time to equilibrium was less than 20 min. Kinetic study of most of the FeCl₃-AC adsorption occurred at the first 1 hour, followed by a relatively slow adsorption process. The FeCl₃-AC demonstrates larger adsorption rate compared with unmodified carbon. Figure 3 shows the removal of nitrate as a function of adsorbent dosage.

In general, increase in adsorbent dosage increased the percent removal of nitrate, which is due to the increase in adsorbent surface area of the adsorbents. The results clearly indicate that the removal efficiency increases for AC, but it has not significant effect on FeCl₃-AC. The results were shown removal of FeCl₃-AC may be dependent to surface chemistries. An understanding of AC adsorption processes requires knowledge of adsorbent properties, including its respective characteristics and surface chemistries such as pore size distribution and surface functional groups[10]. Presence of FeCl₃ enhanced the mesopore area and hence the adsorption. The AC mainly with micropore had the least special surface area and pore volume in all samples. After heat activation with FeCl₃, the special surface area of FeCl₃-AC was increased. This implied that the activation by heating with FeCl₃ could effectively promote the mesopore development. In heating process, the particles of FeCl₃ would immigrate and aggregated to larger particles, which could blocked some micropores, entered and narrowed the mesopores size to form micropore, so, the mesopore volume markedly decreased and the micropore volume changed less. The SEM images of samples were displayed in figure 2.

The surface of AC was smoothing and with some grooves that formed during filature, some particles on the surface were the adsorbed dirt. The FeCl₃-AC surface was more coarseness and the wide of groove widen because the activation processing was the echoed and burnt of carbon. The different pore structure could affect on the nitrate adsorption by modified AC. There appeared some particles with clamp shape on the surface of FeCl₃-AC, this indicated that the iron was reduced and aggregated to larger particles. TABLE 1 shows the ACs specific surface area and the cumulative pore size distribution determined by mercury porosimeter analysis.

It can be seen that following the treatment procedures, more carbon was burned off from the com-
TABLE 1: Some physicochemical characteristics of almond AC and FeCl$_3$-AC

<table>
<thead>
<tr>
<th>Parameter</th>
<th>AC</th>
<th>FeCl$_3$-AC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total specific surface area (m$^2$/g)</td>
<td>1165</td>
<td>2680</td>
</tr>
<tr>
<td>Total porosity (cm$^3$/g)</td>
<td>12.25</td>
<td>8.14</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
<td>46.04</td>
<td>41.26</td>
</tr>
<tr>
<td>Apparent (Bulk) Density (g/ml)</td>
<td>0.419</td>
<td>0.417</td>
</tr>
<tr>
<td>Iodine number (mg/g)</td>
<td>260</td>
<td>375</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>3.30</td>
<td>7.55</td>
</tr>
<tr>
<td>pH</td>
<td>3.72</td>
<td>2.72</td>
</tr>
</tbody>
</table>

TABLE 2: Water quality after contact with AC and FeCl$_3$-AC

<table>
<thead>
<tr>
<th></th>
<th>AC-0</th>
<th>AC-FeCl$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.71</td>
<td>5.5</td>
</tr>
<tr>
<td>Nitrite (mg/l)</td>
<td>0.0175</td>
<td>0</td>
</tr>
<tr>
<td>Ammonia (mg/l)</td>
<td>0.72</td>
<td>0.32</td>
</tr>
<tr>
<td>Chloride (mg/l)</td>
<td>137</td>
<td>162</td>
</tr>
<tr>
<td>Sulfate (mg/l)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fe (µg/l)</td>
<td>2000</td>
<td>500</td>
</tr>
</tbody>
</table>

CONCLUSION

This study shows that FeCl$_3$-AC was found to be an effective agent for nitrate removal. The loaded FeCl$_3$ on AC supports could improve the adsorption capacity of nitrate removal due to chemical reaction and adsorption. According to the results, it was suggested that nitrate were adsorbed onto the FeCl$_3$ impregnated AC via the mechanism, the nitrate was leached from the impregnated carbon, followed by the formation of a FeCl$_3$ nitrate complex, and the subsequent adsorption of the complex on the carbon.
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REFERENCE