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Effect of Coagulation Process in Presence of Chitosan and Psyllium Plantago in Removal of Perchlorate at High Concentrations

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In this study, the efficiency of coagulation process for removal of perchlorate at high concentrations from aqueous solution was investigated. The effect of various parameters such as coagulant dosage, solution pH and initial perchlorate concentration on process efficiency was also studied. Moreover, the effect of both chitosan and psyllium plantago as natural coagulant aids in coagulation process for removing perchlorate was studied. The results showed that ferric chloride was better in perchlorate removal than that of aluminum sulfate. Moreover, the use of chitosan and plantago as coagulant aids led to an increase in removal efficiency of perchlorate in coagulation process (78 and 77.5 %, respectively). Thus, the results indicated that the coagulation process can be used as an effective approach in perchlorate removal at high concentrations. Moreover, the use of both chitosan and plantago as coagulant aids led to an increase in removal efficiency of perchlorate by coagulation process. Therefore, these compounds can also be used as natural adsorbents in removal of perchlorate.

Keywords: Perchlorate, Coagulation, Electrocoagulation, Chitosan, *Plantago psyllium*.

INTRODUCTION

Perchlorate is the inorganic anion that consists of four oxygen atoms and one chlorine atom. When its salts are solvated in water, it can release in the environment. Perchlorate is a strong oxidant that is explosive and very stable in the environment [1]. Basically, perchlorate found in the environment can be either naturally or artificially produced. Natural sources are including mining and ore containing rich deposits of sodium nitrate. Artificial sources include the production and storage of solid fuel for missiles, rockets, weapons and combustion and detonation for the disposal of products containing perchlorate [2]. Perchlorate salts are widely used as the oxidizer in solid rocket fuel. Since this compound has a limited life span, fuels containing perchlorate must be changed periodically to fresh ones. Therefore, perchlorate can be discharged into the environment. This widespread application can also lead to the release of perchlorate into the groundwater. It has been reported that the most of the perchlorate contamination in groundwater is attributed to the manufacturing of solid rocket fuel by the department of defense [1,3]. Exposure to perchlorate causes hypothyroidism. The thyroid gland is the primary target of perchlorate toxicity in humans. Previous studies reported that exposure to high doses of perchlorate can result in the decrease of body weight, cause hypertrophy of the thyroid gland and decrease in gene expression of thyroglobulin [4]. Considering its adverse effects on human, the EPA set a drinking water equivalent level of 24.5 μg/L [5]. Nowadays, several technologies have been studied for treatment of contaminated water with perchlorate such as biological, adsorption and membrane processes. Some disadvantages of these processes (*e.g.* low efficiency at high concentrations of perchlorate, low capacity, high operational cost and clogging) make them impractical in large-scale usage [6,7]. Chemical coagulation process is one of the most commonly used processes for removing various pollutants from water and wastewater in many part of the world. In this process different metal coagulants (based on aluminum and on iron) are used. On the other hand, in the chemical coagulation process the use of natural coagulant aids has now been taken more and more into consideration [8,9]. Chitosan is a non-toxic polymer that can be used as a natural coagulant aid.

It is biodegradable, environmentally friendly, low cost and availability of renewable resources [10]. Moreover, plantago psyllium is a natural polymer that is non-toxic and according to the literature, has no adverse effects on human [11].

The aim of this study was to investigate the effect of coagulation process in the presence of chitosan and psyllium plantago for perchlorate removal at high concentrations. Moreover, the effect of some operational parameters such as coagulant concentration, pH, perchlorate concentration, chitosan concentration and plantago psyllium concentration on the removal efficiency of perchlorate was studied.

EXPERIMENTAL

The perchlorate was purchased from Merck. Ferric chloride and aluminum sulfate were obtained from Merck.

Experiments were carried out in semi-jar test reactors. The laboratory scale batch reactors were made of plexiglass. In the first step of experiments, the efficacies of two coagulants (ferric chloride and aluminum sulfate) were assessed in four coagulant concentrations (10, 20, 40 and 60 mg/L) in removal of perchlorate. In the next step, in order to study the effect of pH of the solution on the process efficiency, the experiments were carried out in three different values of pH (5, 7 and 9). Moreover, the effect of perchlorate concentration on the coagulation efficiency was studied in the range 10 to 1000 mg/L. After determining optimum conditions, the effect of chitosan as a natural coagulant aid in coagulation process was tested in the range 2 to 10 mg/L. The effect of plantago psyllium on the coagulation efficiency in perchlorate removal was tested in the above mentioned range.

Analysis: The solutions of 10 and 100 μg mL^{-1} were prepared by dissolving the solution of 1000 mg/L in a certain volume of distilled water. A certain volume sample was transported into a centrifuge pipe and 1 mL of sulfuric acid and 1 mL of methylene blue were added to the each sample. The volume of centrifuge pipe sample was reached to 9 mL by adding distilled water. Then, the sample was centrifuged for 5 min. Next, 1 mL of chloroform solvent was added into the sample. In order to extract the ion pair formed, the sample was centrifuged for 5 min. Finally, the supernatant solution was removed and the underside of the solution was transported into a micro-cell. The perchlorate concentrations were measured using a UV-visible spectrophotometer (DR 5000) at λ_{max} = 652 nm wavelength [12].

RESULTS AND DISCUSSION

In first step of the study, the effect of coagulant concentrations on the removal efficiency of perchlorate was investigated. The removal process efficiency increased from 50.4 to 53.1 % with increasing aluminum sulfate concentration from 10 to 20 mg/L (Fig. 1). This can be related to the role of aluminum sulfate as a coagulant. Because aluminum salts generate a series of metal hydrolysis species in water solution. The metal hydrolysis can precipitate the particles and collides in water environments. Moreover, perchlorate could be removed by adsorption onto the metal hydroxide hydrolysis products that are formed. On the other hand, by increasing aluminum sulfate more than 20 mg/L, the process efficiency decreased.

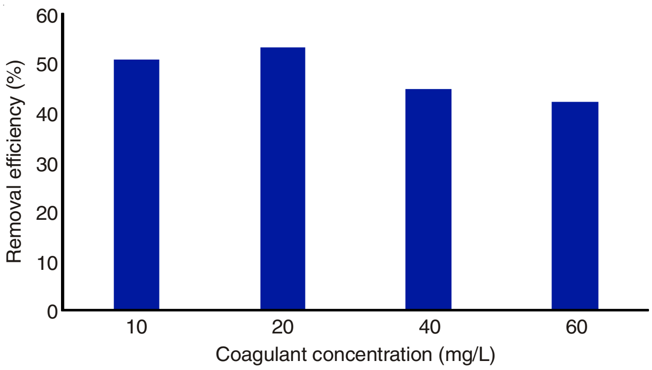

Fig. 1. Effect of aluminum sulfate on coagulation process in perchlorate removal (pH 7, initial perchlorate concentration 1000 mg/L, rapid mixing time 30 s and slow mixing time 30 min)

The minimum removal efficiency of perchlorate was equal to 40 % and was seen at the highest concentration of aluminum sulfate (60 mg/L). A similar trend was also observed with ferric chloride. Due to the higher efficiency of ferric chloride compared with aluminum sulfate, ferric chloride was selected as optimum coagulant for following experiments (Fig. 2). This phenomenon may be related to the negative effect of aluminum at high concentrations. A high concentration of aluminum in treated water gives rise to turbidity and can reduce removal pollutant efficiency. Results of a study carried out by Ghodbanan [13] on treatment of cellulosic effluents using combination of chemical coagulation and biological process confirm our results [13,14].

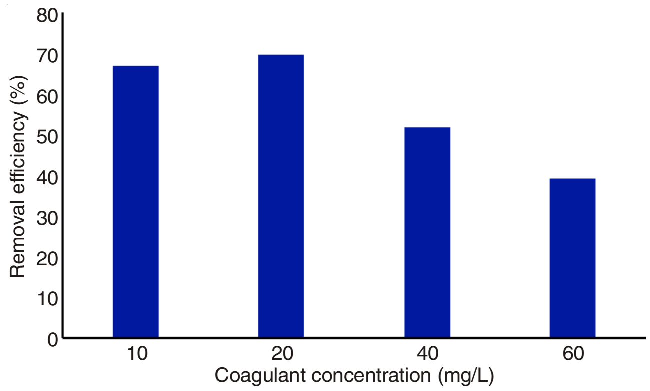

Fig. 2. Effect of ferric chloride on coagulation process in perchlorate removal (pH 7, initial perchlorate concentration 1000 mg/L, rapid mixing time 30 s and slow mixing time 30 min)

The effect of pH on the coagulation process with ferric chloride as coagulant was investigated in the range 5-9 (Fig. 3). According to the obtained results, variation in pH of the solution has obviously effect on the coagulation process in removal of perchlorate. So that, the coagulation efficiency decreased with increasing pH of the solution. In this step of the experiments, the maximum removal efficiency was 69.6 % and was seen at pH 5. By contrast, the minimum removal efficiency was seen at pH, which was equal to 33.6 %. The effect of pH on the coagulation process efficiency in perchlorate removal can be related to the isoelectric point variation synchronize with pH variation. Because in chemical coagulation process at pH values lower than isoelectric point, produced iron or aluminum hydroxides and polymers have positively

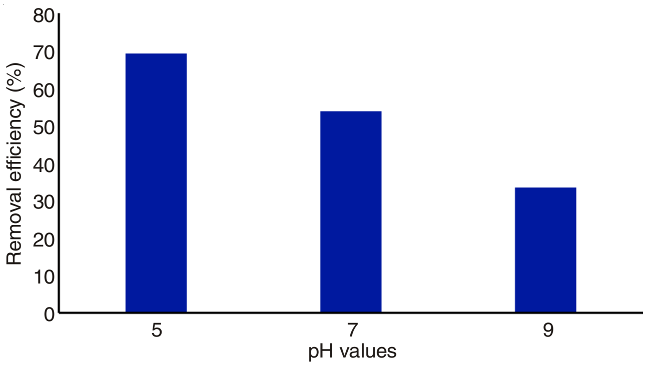

Fig. 3. Effect of pH on coagulation process in perchlorate removal (initial perchlorate concentration 1000 mg/L, rapid mixing time 30 s and slow mixing time 30 min)

charged [15]. Therefore, the negative perchlorate ions are easily absorbed and eliminated by produced flocs. Similar results were obtained by Ashery *et al.* [16] on the effect of pH on the coagulation process in removal of natural matter and turbidity. Hering *et al.* [17] reported that the optimal pH range for arsenic removal is from 5 to 7.

Initial pollutant concentration is one of the other important factors in coagulation process. In this study, the effect of different perchlorate concentrations (10, 100 and 1000 mg/L) on the coagulation process was investigated under same conditions. The coagulation efficiency in removal of perchlorate decreased with the increase of concentration of perchlorate. The maximum removal efficiency was achieved in perchlorate concentration of 100 mg/L, which was equal to 72.5 % (Fig. 4). In contrast, the minimum removal efficiency was achieved in perchlorate concentration of 10 mg/L, which was 44.4 %. This could be attributed to the probability of adsorption and collision between produced metal hydroxides and perchlorate ions. Because the high concentration of perchlorate increases the probability of collision between produced metal hydroxides and perchlorate ions.

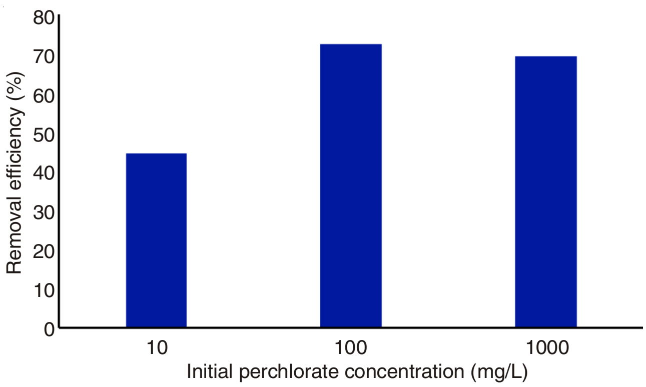

Fig. 4. Effect of initial perchlorate concentration on coagulation process in perchlorate removal (pH 7, initial perchlorate concentration 1000 mg/L, rapid mixing time 30 s and slow mixing time 30 min)

Chitosan is a natural and non-toxic cationic polyelectrolyte. In this study in order to increase the coagulation efficiency, three chitosan concentrations of 2, 5 and 10 mg/L was applied as a coagulant aid under optimum conditions. As shown in Fig. 5, chitosan led to an increase in the coagulation

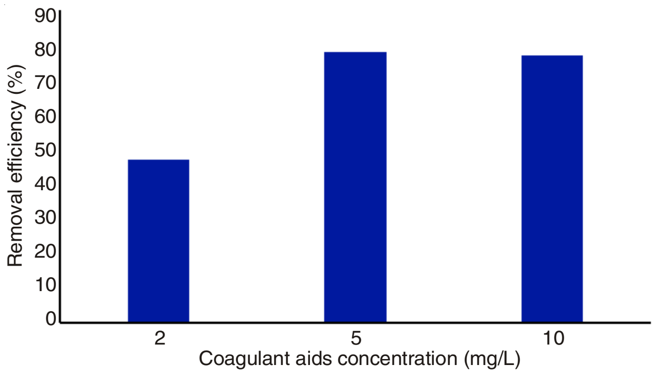

Fig. 5. Effect of chitosan concentration on coagulation process in perchlorate removal (pH 7, initial perchlorate concentration 1000 mg/L, rapid mixing time 30 s and slow mixing time 30 min)

efficiency in perchlorate removal. According to the obtained results, the use of chitosan led to an increase in coagulation efficiency in removal of perchlorate. Moreover, the process efficiency increased from 47 to 77 % with increasing chitosan dosage from 2 to 7 mg/L. This result can be due to the characteristics of the chitosan polymers. Because chitosan contains a large number of amino groups and spiral structures that can increase the coagulation efficiency by sedimentation and adsorption of the pollutant [18]. On the other hand, the chitosan polymer has positive charge at natural pH ranges. So it can attract negative perchlorate ions in this pH ranges. In contrast, by increasing chitosan concentration (more than 5 mg/L) the removal efficiency decreased. Psyllium plantago was used as a coagulant aid in coagulation process with ferric chloride. A similar trend was observed for plantago as coagulant aid. The effect of three plantago concentrations in the mentioned range was studied under optimum conditions. Results indicated that the plantago has a positive effect on perchlorate removal by coagulation process. As shown in Fig. 6 the use of plantago increased the coagulation efficiency increased from 43.7 to 74.9 % with increasing plantago concentration from 2 to 5 mg/L. This increase can be attributed to the plantago polymer. The properties of plantago (polymer structure) allow the process to increase the removal efficiency of perchlorate. In contrast, by increasing plantago concentration (more than 5 mg/L) the removal efficiency decreased. This is in line with the finding of the previous study [10].

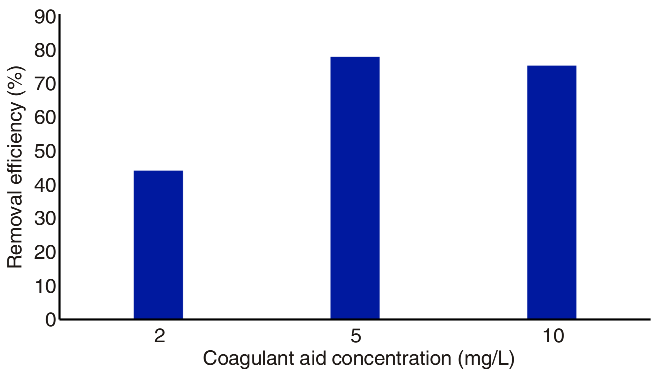

Fig. 6. Effect of plantago concentration on coagulation process in perchlorate removal (pH 7, initial perchlorate concentration 1000 mg/L, rapid mixing time 30 s and slow mixing time 30 min)

Conclusion

The efficiency of coagulation process in removal of perchlorate at high concentrations from aqueous solution was investigated. The effect of various parameters such as coagulant dosage, solution pH and initial perchlorate concentration was also studied. Moreover, the effect of chitosan and psyllium plantago as two natural coagulant aids in the coagulation process for removing perchlorate was investigated. According to the results, the ferric chloride was better in removal of perchlorate than that of aluminum sulfate. Moreover, the use of chitosan and plantago as coagulant aids led to the increase of perchlorate removal efficiency in coagulation process (78 % and 77.5 %, respectively). Results indicated that coagulation process in perchlorate removal in high concentration can be used as an effective process. Moreover, both chitosan and plantago can be used as natural adsorbents in removal of perchlorate.

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