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RESEARCH ARTICLE - CHEMISTRY

Removal of Nitrate and Phosphate from Water by Clinoptilolite-Supported Iron Hydroxide Nanoparticle

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Abstract In this study, we used clinoptilolite-supported iron hydroxide NPs ($Fe(OH)_3/Cp$) for evaluating the simultaneous removal of NO_3^- and PO_4^{-3}. Remediation was investigated in a range of initial concentrations of NO_3^- (0–25 mg/L) and PO_4^{-3} (0–25 mg/L) as a function of pH (2–8), nanoparticles concentration (1 and 0.5 g/L). To achieve the best result, the weight ratio of raw material in iron sulfate versus clinoptilolite (5:1, 2:1, 1:1, 2:1) was tested. The highest pollutant removal was obtained 93% for PO_4^{-3} in 5:1 ratio of Fe versus clinoptilolite and 81% for NO_3^- in 1:2 ratio of Fe versus clinoptilolite at the pH of 2. Kinetic data for NO_3^- and PO_4^{-3} were well fitted in the pseudo-first-order model and pseudo-second-order model, respectively. Based on the results, it may be concluded that $Fe(OH)_3/Cp$ NPs can effectively be used for simultaneous removal of NO_3^- and PO_4^{-3} from water resources.

Keywords Nitrate · Phosphate · Iron hydroxide NPs · Clinoptilolite · Eutrophication · Remediation · Pollution

1 Introduction

Although industrial and technological developments have made life easier in many aspects, they have also caused some losses. The pollution of environmental elements results from chemicals value increase or energy level rise [1]. Nitrate ion (NO_3^-) is a contaminant which has reportedly been observed in surface and underground waters in many parts of the world. The underlying factors of NO_3^- increase in soil and water resources are industrial, stockbreeding and agricultural activities [2,3]. The global demand for NO_3^- is reported to be about 155 million in 2016 which part of it enters to the surface water and groundwater resources through the water output from the fields and deep penetration [4].

The industrial livestock farms also have a role in increasing NO_3^- in water resources. Moreover, the urban and industrial wastewaters are also considered as important sources in increasing NO_3^- in water and soil resources. Among the most significant effects on humans, one can point to blue baby syndrome and stomach cancer [5–8]. Another effect of NO_3^- on water is the enrichment of surface waters that causes rapid growth of harmful aquatic plants and undesired plankton growth [5,9]. The shortage of vitamin A and reproductive disorders such as abortions and decreased milk production are among the effects of NO_3^- in drinking water of livestock. In order to control the side effects of NO_3^-, Environmental Protection Agency (EPA) of America has announced 45 mg/L as the maximum allowable density of NO_3^- in drinking water (equivalent to 10 mg of nitrogen per liter) [8].

Various ways to eliminate or reduce the NO_3^- concentration in water have been developed. These methods

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include chemical, physical and biological processes, like biological denitrification, ion exchange, reverse osmosis, electro-catalytic, and chemical restoration. The mentioned methods are economically expensive and inefficient [8].

In addition, the large amounts of phosphate same as nitrate in the aquatic environments may cause abnormal algae and aquatic plants growth which result in water quality reduction and changes in taste, color, loss of biodiversity, and eventually eutrophication phenomenon [10]. For eutrophication to occur, various phosphorus concentrations ranging from 0.005 to 0.05 mg/L are required [11]. The standard levels of PO_4^{3-} in drinking water and industrial wastewaters are reported to be 0.2 and 0.6 mg/L, respectively [12,13]. Agricultural activities such as excessive use of PO_4^{3-} fertilizers, industrial wastewaters and aerial exposure of minerals are the most common ways of phosphorus entry into soil and water resources [14]. The agricultural activities are the main sources of pollution [15]. Not only does excessive consumption of PO_4^{3-} fertilizers reduce yields but also, because of causing disorder in nutrients absorption, they cause reduction in the absorption of some nutrients and in long run they negatively affect the yield efficiency [16]. Global demand for phosphorus element is expected to be 51/6 million tons in 2016 [4]. So far, several methods for phosphorus removal from wastewaters and polluted waters have been applied. Chemical and biological methods are the most important of them. However, among the disadvantages of chemical methods, expensive chemicals and low efficiency could be noted. Moreover, the deficiencies of biological methods are difficulty of biological process and possible restoration of phosphorus into water resource [17,18].

Nanotechnology is an effective method to remove environmental pollutants. This method is fast, easy and affordable [19–21]. Among the nanoparticles(NPs), zero-valent iron nanoparticles (NVZI) with their unique characteristics such as small size, distinctive surface area and significantly high reactivity have the high capacity to remove environmental pollutants such as nitrate and phosphate [22,23]. Despite of their benefits, NVZIs have little persistence during reaction [24], they rapidly oxidizes when exposed to air and during a chemical reaction these NPs accumulate and their proper operating level reduces [25,26].

In some studies, few amorphous Fe oxides and hydroxides with low-grade crystalline [27], geotite [28], combinations of two or more metal oxides such as Fe and Al oxides and hydroxides [29], binary Fe-Mn oxides [30], binary oxides of zirconium Fe [31], Fe-lanthanum hydroxide with activated carbon [32], ternary oxide (Fe-Al-Mn) [33], TiO_2, Al_2O_3, and Fe_2O_3NPs [34] and nano-structural Fe-Cu oxide [35] were used to remove the phosphorus.

The major problem with the use of NPs is their supplementation and accumulation during the manufacturing processes which decrease their active surface. To overcome this problem, several methods have been studied such as the use of stabilizers. Some of these stabilizers include resin [36], silicon [37], activated carbon [5], kaolinite [38], carboxymethyl cellulose [8] and Graphene [39], and sand as a stabilizer of the metal NPs to simultaneously remove PO_4^{3-} and arsenic [40]. A novel zeolite/Fe_2O_3 composite material, was produced by using coal fly ash as raw material. The obtained new material was shown to be unique to simultaneously retain cationic (ammonium) and anionic (phosphate) pollutants from water [41].

The present work describes a facile and cost effective method to prepare Recyclable Fehydroxides NPs ($Fe(OH)_3$) stabilized with clinoptilotite (Cp). To our knowledge, it is the first time that $Fe(OH)_3$/Cp NPs is used for simultaneous removal of NO_3^- and PO_4^{3-} from water. Nitrate and phosphate were selected as their high concentrations play a major role in eutrophication.

In this study

- NO_3^- and PO_4^{3-} removal with some special synthesized $Fe(OH)_3$/Cp NPs was investigated.
- The structural characterization of $Fe(OH)_3$/Cp NPs was studied using SEM, XRD and TEM
- Different amount of precursors were investigated to find the maximum efficiency.
- The adsorption kinetics was evaluated with Pseudo-first-order models and Pseudo-second-order models.

This work provides a promising and effective way to the water remediation that have not been reported to date.

2 Experimental

2.1 Synthesis of Nano $Fe(OH)_3$/Cp

5.0 g of $FeSO_4 \cdot 7H_2O$ (98%, Aldrich) was dissolved in 250 mL of 30% technical grade methanol and 70% deionized water (v/v). Then 1.0 g Cp was added and shaked for 60 min. Natural Cp was collected from a mine in Semnan province, central Iran. It was used as a stabilizer for the FeNPsand was grounded to a size of 0.5 mm. The pH was adjusted to 6.8 by 2M NaOH. The mixture was stirred for 20 min and then centrifuged for another 15 min, at 5000 rpm. The solid was washed twice with technical grade methanol. The resulting solid was dried and then broken up with a spatula to form a fine black powder. To detect the maximum efficiency, several other batches of $Fe(OH)_3$/Cp NPs with different amount of precursors; $FeSO_4 \cdot 7H_2O$ relative to Cp particles, including 5:1, 2:1, 1:1, 1:2 ratios (w/w) were used.

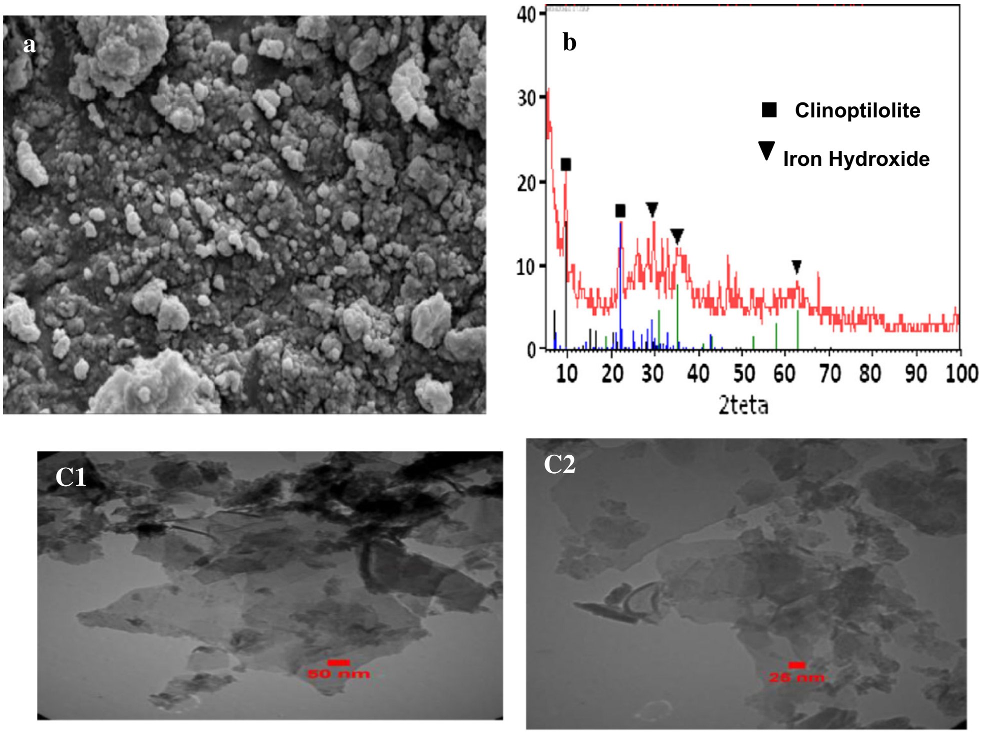

Fig. 1 SEM image **a** XRD pattern **b** TEM images of the nano $Fe(OH)_3$/clinoptilolite (C_1/C_2)

2.2 Characterization of the Nanoparticles

The particle size and morphology were investigated by PHILIPS (EM208S, the Netherlands) transmission electron microscopy (TEM) at 100 kV of acceleration voltage and scanning electron microscopy (SEM) of the Holland Philips EM3200 microscope with an accelerating voltage of 26 kV. Crystal structures were examined using a Holland Philips Xpert X-ray powder diffraction (XRD) diffractometer (Cu K, radiation, $\lambda = 0.154056$ nm).

2.3 Phosphate and Nitrateremoval

In this experiment, the removal rate of NO_3^- and PO_4^{3-} by $Fe(OH)_3$/CpNPs was examined. In this regard, various solutions with different concentrations of NO_3^- (0–25 mg/L) and PO_4^{3-} (0–25 mg/L) were prepared and treated with fixed concentration of NPs. After the equilibrium time, the remaining amounts of NO_3^- and PO_4^{3-} in the solutions were measured. The difference between the initial and final concentration was used in order to determine the removal level. The required NO_3^- and PO_4^{3-} were prepared from potassium nitrate (KNO_3) and potassium dehydrogen phosphate (KH_2PO_4), respectively. Ionic strengths of the solutions were adjusted by KCl (0.01 M). The suspension pH was set at (2,4,6,8) by 0.1 M hydrochloric acid (HCL)and buffered by adding 0.2 M of acetic acid(CH_3COOH).The NO^{3-} and PO_4^{3-} equilibrium concentrations were measured by UV–Vis spectrophotometer at 220 and 820 nm wavelengths, respectively. After measuring the remaining concentrations of NO_3^- and PO_4^{3-} in the solutions, decrement in concentrations of PO_4^{3-} and NO_3^- was considered as removed concentration.

3 Results and Discussion

3.1 Characterization of Nanohydroxid Fe\Cp

Nanomaterials used as adsorbent were characterized by SEM (Fig. 1a) and X-ray Diffraction (XRD) (Fig. 1b). The mean pore diameters of $Fe(OH)_3$/Cp NPs were 44.2 nm. Synthesized $Fe(OH)_3$/Cp NPs was analyzed by XRD. Its Cp component showed two diffraction peaks at 9.45o and 21.98°. In addition, three diffraction peaks at $2\theta = 30.808°$, 35.023° and 62.728° with the index of (1 1 1) and (4 4 0) indicated the formation of Fe hydroxide Fig. 1b. Using the Scherrer formula [42], the mean pore diameter of $Fe(OH)_3$/Cp NPs was found to be 44.2 nm.

3.2 Equilibration Time

Contact Time and Sorption Kinetics

To determine the appropriate equilibration time, the removal of PO_4^{3-} and NO_3^- was examined by $Fe(OH)_3$/Cp

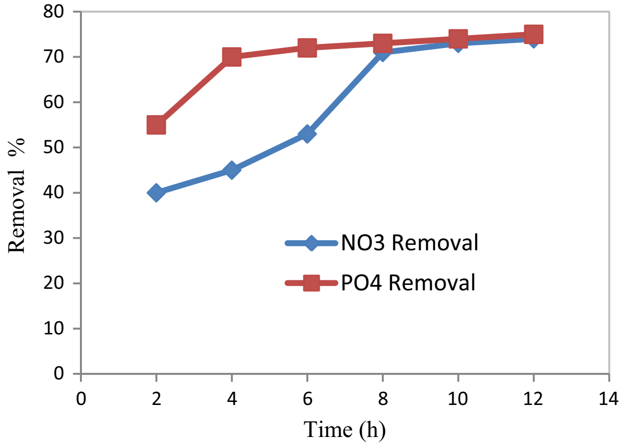

Fig. 2 Effect of contact time on the adsorption of phosphate and nitrate ions

NPs at different distinct times (2, 4, 6,8,10, 12 h). NO_3^- removal was initially fast so that in the first 8 hours 71percentage of NO_3^- was removed. Then the NO_3^- removal was constant in the next four hours. The PO_4^{3-} reaction with the absorption was fast at first and more than the NO_3^- removal; however, throughout the process it gradually increased Fig. 2. The difference between the two ion balance time could be due tomore PO_4^{3-} willingness than NO_3^- to substitute for hydroxyl ion on the surface of iron hydroxide $Fe(OH)_3$ NPs. This experiment had three replications.

Previous studies have indicated that P sorption increases with time [37,41]. Thus, depending on the type of material used, sorbent concentration, initial P concentration, equilibrium time may be reached after various times elapsed [43].

The pseudo-first model was used in the kinetic Studies (Eq. 1) [44]. Parameters (K_1, Q_e, Q_t) were calculated by using experimental data which were fitted to the model (Table 1).

$$\frac{\mathrm{d}Q_t}{\mathrm{d}t} = K_\mathrm{I}(Q_\mathrm{e} - Q_\mathrm{t}) \tag{1}$$

The Q_e and Q_t are the amount of adsorbed NO_3^- or PO_4^{3-}, respectively, on the adsorbent in the equilibrium time and time t. The K_I is the absorption rate constant. With the integration of the above equation and rearranging it, the resulting equation will be as follow (Eq. 2):

$$\ln(Q_\mathrm{e} - Q_\mathrm{t}) = -K_\mathrm{I}t + \ln Q_\mathrm{e} \tag{2}$$

According to the correlation coefficient 0.93–0.94, it could be concluded that linear regression is adequate to describe the experimental data. However, the whole calculated Q_e values for PO_4^{3-} was much smaller than the practical Q_e (calculated through the experiments). Therefore, although the first model is fully practical to describe the data but it doesn't have the necessary accuracy to predict the Q_e. Therefore second-order model was used to explain PO_4^{3-} adsorption with the equation as follow (Eq. 3) [45]:

$$Q_\mathrm{t} = \frac{k_\mathrm{II} Q_\mathrm{e}^2 t}{1 + k_2 Q_\mathrm{e} t} \tag{3}$$

The pseudo-second-order model describes PO_4^{3-} removal by NPs stabilized on Cp which R_2 coefficient is 0.99. The calculated Q_e amount is near the practical Q_e amount (resulted from the experiment). Therefore, the kinetics of pseudo-second-order model states the PO_4^{3-} uptake better than the pseudo-first-order model (Table 2).

3.3 Effect of Nano $Fe(OH)_3$\Clinoptilolite Concentrations on Remediation

NO_3^- and PO_4^{3-} reduction as a function of the initial concentration of these ions (0–25 mg) using two NPs concentrations of 0.02 and 0.04 g was performed. The results showed the highest removal rate of NO_3^- and PO_4^{3-} in the initial concentration of 5 mg per liter, pH of 2 and 0.04 g adsorbent were 90% and 80%, respectively. However, with using 0.02 g adsorbent, ion removal rates both declined. Removal rate for PO_4^{3-} and NO_3^- were 76 and 70%, respectively, Fig. 3

Table 1 Parameters of pseudo-first-order models

	Pseudo-first-order kinetics				Initial concentration
	R^2	KI (min^{-1})	Qe** (mg g^{-1})	Qe* (mg L^{-1})	(mg L^{-1})
5–1	0.959	0.3762	8.717848	6.1	NO_3^-
2–1	0.9581	0.2843	5.388918517	6.4	
1–1	0.9341	0.3944	11.84179	7.5	
1–2	0.9613	0.3519	9.719552	8.2	
5–1	0.9266	0.3019	4.388875	7.1	PO_4^{3-}
2–1	0.886	0.2792	4.501432	7.5	
1–1	0.9138	0.2693	2.598611	8.8	
1–2	0.9385	0.2687	2.486837	9.4	

Table 2 Parameters of pseudo-second-order models

PO_4^{3-}	Pseudo-second-order kinetics				Initial concentration
	R^2	KII (min^{-1})	Qe** (mg g^{-1})	Qe* (mg L^{-1})	10 (mg L^{-1})
5–1	0.9967	0.09151758	10.1626016	7.1	
2–1	0.9956	0.114863734	9.22509225	7.5	
1–1	0.9991	0.173270077	7.96812749	8.8	
1–2	0.9987	0.167753383	7.48502994	9.4	

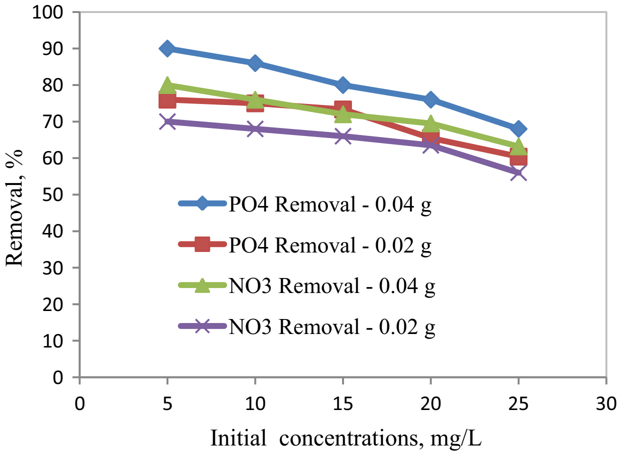

Fig. 3 Effect of $Fe(OH)_3$/Cp NPs concentration on phosphate and nitrate removal from water (0.01M KCl, pH = 2)

With increasing the adsorbent concentration, the contact surface with the pollutants increased, resulting in more elimination. Increasing the concentration of Fe NPs had a greater impact on the PO_4^{3-} to NO_3^- removalwhich may be due to a greater tendency of PO_4^{3-} to bond with Fe than NO_3^-.

3.4 Effect of pH on the Removal of Pollutants

The solution contained the same concentration of NO_3^- and PO_4^{3-} and was prepared from KNO_3 and KH_2PO_4 salts. 0.04 g adsorbent with 40 mL equal to (1 g/L) of the above solutions was placed in 50 mL polyethylene containers. The pH of the suspension was adjusted by using 0.1 M of HCl and 0.1 M NaCl. Figure 4 illustrates the remediation of pollutants as a function of pH at pH 2, 4, 6 and 8. The PO_4^{3-} and NO_3^- initial concentrations were (5, 10, 15, 20, 25 mg/L).

The data showed an adverse relation between the initial pH values and the amount of remediation from the solution. The trends were similar to observation in the NO_3^- and PO_4^{3-} solutions. The removal of PO_4^{3-} decreased as the pH increased.

However, this decline rate was more pronounced for NO_3^- than PO_4^{3-}. It means NO_3^- is more sensitive to pH alterations and more dependent on it. This fact is demonstrated by experimental data in Fig. 4a, b. Maximum percentage of PO_4^{3-} removal (90%) could be achieved at pH = 2. PO_4^{3-} could be replaced with hydroxyl ions on Fe hydroxide and Cp surfaces. PO_4^{3-} tendency to succeed with hydroxyl is more than the NO_3^-. Maximum percentage of NO_3^- (80%) removal was also achieved at pH = 2.

Increased the pH from 2 to 8 causes an approximately linear decreased in the ability of Fe NPs for removing nitrate from water containing different concentrations of nitrate [46]. Xie et al. [41] indicated that the removal of phosphate increased with decreasing pH while that of ammonium showed an opposite behavior. It was found that neutral pH condition could favor the uptake of both ammonium and phosphate.

Nitrate removal may be rationalized by considering the consumption of $[H^+]$ through removal of $[NO_3^-]$ [47], and/or the release of hydroxyl group and the increase in solution pH [48].

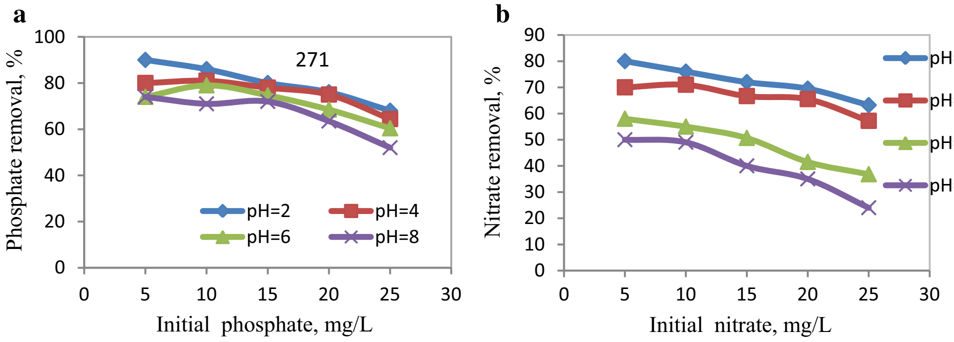

Fig. 4 Effects of pH on the % phosphate removal (**a**) and % nitrate removal (**b**) by $Fe(OH)_3$/Cp NPs (0.04 g/40 mL), KCl = 0.01M (ionic strength)

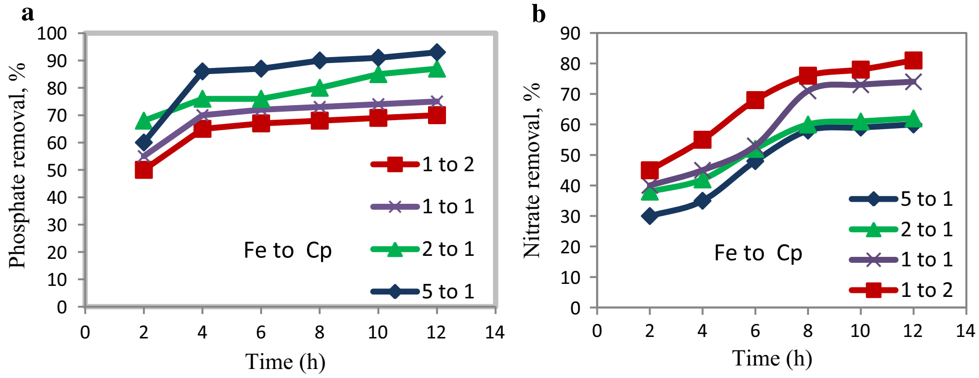

Fig. 5 Effects of Fe/Cp ratio on the % phosphate removal (**a**) and % nitrate removal (**b**) by $Fe(OH)_3$/Cp NPs (0.04 g/40 mL), KCl = 0.01 M (ionic strength)

3.5 Effect of Fe to Clinoptiloliteratio

In order to achieve the best removal efficiency, Fe $(OH)_3$/Cp were synthesized with different weight ratios of raw material Fe sulfate to Cp (5: 1, 2: 1, 1: 1, 1: 2) and the removal efficiency of NO_3^- and PO_4^{3-} were studied.As illustrated in Fig. 5, much higher efficiency for NO_3^- removal was obtained by decreasing the Fe/Cp ratio. The maximum efficiency was found when Fe to Cp with 1:2 ratio was used. It turned out that the positive effect of Cp was related to a better dispersion of $Fe(OH)_3$ NPs by having small pores in its structure, and thus producing higher reactive surface area. For PO_4^{3-} on the other hand, much higher removal was obtained by increasing the Fe to Cp ratio, as maximum efficiency was obtained by Fe to Cp with 5:1 ratio. Due to PO_4^{3-} tendency to be more absorbed on the surface of Fe particles compared to NO_3^-, to remove PO_4^{3-} the Fe concentration is more important than the Cp concentration.

4 Conclusions

Wastewater always contains lots of coexisting anions, which could potentially compete with $PO4^{-3}$ for the adsorption sites. $Fe(OH)_3$/Cp effectively removes NO_3^- and $PO4^{-3}$ simultaneously often through absorption and anion-exchange reactions in acidic environments in contaminated waters. Replacement of hydroxyl (OH^-) and PO_4^{-3} helps to improve the reaction. In addition Cp with its porous structure can accommodate NO_3^- and $PO4^{-3}$ in itself and thereby helps to remove the environmental pollutants. The results of this experiment indicated that the amount of adsorbed NO_3^- slightly decreased in the presence of PO_4^{3-}. Most of the PO_4^{3-} and NO_3^- simultaneous removal was achieved in pH of 2 and 90 percent for PO_4^{3-} and percent 80 for NO_3^- were obtained. The elimination of NO_3^- and PO_4^{3-} decreased with the increase in pH. The highest PO_4^{3-} removal was in the ratio of 5–1 (Fe/Cp) and the highest amount of NO_3^- removal was in a ratio of 1 to 2 (Fe/Cp), respectively. By increasing the weight ratio of Cp to iron, phosphate removal increase and adversely nitrate removal rate decreases. These particles are effective in removing environmental pollutants in areas where the eutrophication phenomenon has occurred.

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