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Treatment of wastewater contaminated with Cd(II)–NTA using Fe(VI)

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ABSTRACT

The aim of the present investigation is to assess the applicability of Fe(VI) in the treatment of simulated wastewater contaminated with Cd(II)–nitrilotriacetic acid (NTA) soluble species as a cleaner and greener treatment technology. Initially, the degradation of NTA was observed in a single system treatment reactor that applied varied doses of NTA. Results were correlated with the change in Fe(VI) concentration measured by UV–visible spectrophotometer. As a next step, the Fe(VI) was introduced in the reaction reactor containing Cd(II)–NTA species as to investigate the degradation of NTA measured with the help of change in total organic carbon (TOC). The NTA degradation was observed by using the TOC values obtained at different time intervals at pH 10.0. Moreover, the treated samples were subjected to the change in total cadmium concentration as to observe the simultaneous removal of cadmium from the aqueous solutions. The reactivity of the Fe(VI) was also assessed varying the pH from 8.0 to 12.0 in the treatment of Cd(II)–NTA solution.

Keywords: Fe(VI); Cd(II); NTA; Oxidation; Reduction

1. Introduction

One of the increasing concerns in the treatment of wastewaters perhaps comes from the metal complexed contaminants because of its stability and mobility in aqueous media. Several industrial processes are reported to include the wide use of chelating agents such as nitrilotriacetic acid (NTA), iminodiacetic acid, ethylenediaminetetraacetic acid, etc. These chelating agents show strong affinity towards several toxic heavy metal ions and readily form stable complexes with these metals in aqueous solutions. The degradation of these complexed species was found to be a daunting task in the wastewater treatment technology.

NTA is an important chelating agent which shows several industrial applications. It is extensively used for scale control in cleaners, water softening and in laundry detergents as a builder to replace phosphates. The use of NTA was restricted by legislation in some countries owing to their contribution to the eutrophication of lakes and ponds. In Western Europe, at least 80% of NTA is used in detergents. It is widely used as an eluting agent in purification of rare-earth elements, as a boiler feed-water additive, in water and textile treatment, in metal plating and cleaning, and in pulp and paper processing [1]. It is present in drinking water primarily in the form of metal complexed form, rather than as the free acid. The amount of NTA complexed with metal ions is dependent on the concentrations of

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the metal ion, NTA^{3-} and H^+, as well as the formation constants of the various complexes [2].

On the other hand, cadmium is one of potential environmental pollutant that possessed greater biotoxicity towards humans and animals. In the human body, cadmium accumulates mainly in the kidneys. At high levels, it can reach a critical threshold and can lead to serious kidney failure. Cadmium metal and cadmium compounds are used as pigments, stabilizers, coatings, specialty alloys, electronic compounds, but, most of all (more than 80% of its use), in rechargeable nickel–cadmium batteries. Variety of cost effective materials suggested in the removal of Cd(II) or even other heavy metal toxic ions from aqueous solutions performed under the sorption process seems perhaps an alternative way of waste/effluent treatment [3–9]. However, the removal of metal-complexed species seems to be difficult although few reports intended to employ the materials viz., titaniumoxide in the removal of some heavy metal complexed species from aqueous solutions [10–12].

Further, due to its high chelating capacity, NTA sequesters with metal ions forming metal complexes. It was found that certain NTA complexes (Cu, Ni, Cd, Hg) were very resistant to degradation [13]. Therefore, industrial wastewater containing Cd–NTA complexes need to be treated adequately prior to its discharge into the environment.

Ferrate (Fe(VI)), a higher oxidation state of iron is one of the promising multi-purpose water treatment chemicals because of its novel properties such as high oxidizing capacity (redox potentials, E^0 (FeO_4^{2-}/Fe^{3+}) and E^0 ($FeO_4^{2-}/Fe(OH)_3$ are 2.20 and 0.72 at pH 1 and 14, respectively), selective reactivity, stability as salt forms, and non-toxic decomposition by-products of ferric ion. Since Fe(VI) treatment is not associated with any toxic by-products hence it is termed as a "green compound" and the treatment process is known as "Green Process" [14–17]. Moreover, the by-product of Fe(VI); i.e. Fe(III) is one of potential coagulant/adsorbents hence, could remove other non-degradable impurities from the wastewaters. Therefore, the use of Fe(VI) in the wastewater treatment is multifunctional, it replaces several chemicals frequent to be used in wastewater treatment technology. Owing to this unique multifunctional properties, Fe(VI) has gained enhanced interests for its potential applications in the water treatment technology. Fe(VI) can effectively oxidize several stable organic compounds viz., benzene, chlorobenzene, allylbenzene, phenol, etc. [18–19] along with the inorganic contaminants viz., cyanide, ammonia, etc. [20]. Other studies revealed that Fe(VI) is used as coagulant for removing dissolved color compounds [21]. Although Fe(VI) has been shown to be effective and efficient for the removal of organic and inorganic impurities, only limited studies focused on the metal complexed systems. Yngard et al. attempted the oxidation of weak-acid dissociable cyanides, $Cd(CN)_4^{2-}$ and $Ni(CN)_4^{2-}$, with ferrate [22]. The kinetics of the dissociation of these weak acid dissociable cyanides was discussed with pH range 9.1–10.5 and temperature range 15–45℃. It is suggested that Fe(VI) is effective in removing cyanide in coke oven plant effluent, where organics are also present. The Zn–NTA complex was treated using the Fe(VI). The possible degradation of NTA along with the simultaneous removal of Zn(II) by coagulation/adsorption process was demonstrated. Further, the effect of various background electrolyte concentrations was studied in the treatment method [23].

In view of the above the present study aims to explore the applicability of Fe(VI) in the treatment of wastewater contaminated with Cd(II)–NTA complexes through oxidation of NTA and subsequent removal of Cd(II) by reduced Fe(III) or by precipitation.

2. Methodology

2.1. Materials

The AR/GR grade chemicals were used in this study. Sodium hypochlorite (CAS# 7681-52-9), purified Fe(III) nitrate hexahydrate (CAS# 7782-61-8), potassium hydroxide (CAS# 1310-58-3), *n*-hexane (CAS# 110-54-3), anhydrous ether (CAS# 60-29-7), and methanol (CAS# 67-56-1) were obtained from Merck. Cadmium nitrate tetrahydrate (98%, CAS# 10022-68-1) and NTA (CAS# 139-13-9) were obtained from Sigma–Aldrich. Whatman filter paper (GF/C) (England) and Fritted funnel (10–15 μm) (Merck) were used. Purified water (18 MΩ cm) obtained from Milli Q-Plus Instrument (Millipore SA 67120, Molshiem, France). The stock solutions of cadmium and NTA (1.0 mol/L) were prepared in distilled water, which were further diluted as and when required.

2.2. Preparation of potassium ferrate $K_2Fe^{(VI)}O_4$

Potassium Fe(VI) was prepared by adopting wet chemical oxidation method, with some modifications as described elsewhere [24,25]. In this method, commercially available sodium hypochlorite (12–14%) was used. 300 mL of chilled NaClO solution was taken in a beaker and 90 g of solid KOH was added slowly in this solution and the resulting suspension was cooled. The precipitate formed was filtered with GF/C filter paper, the filtrate received was a clear yellow and highly alkaline NaClO solution. Again the solution was chilled and filtered using a GF/C filter paper to remove any precipitates occurred within the solution. To this solution, 20 g of pulverized ferric nitrate was added slowly within 30 min, with constant and vigorous stirring under cooling conditions (<8˚C). Further, after the complete addition of ferric nitrate, the solution was stirred for another 30 min. It was noted that the cold and highly alkaline conditions favored the oxidation of Fe(III) to Fe(VI). Also the time allowed for stirring may result in enhanced yield, even when using relatively low concentration of NaClO (i.e. 12% NaClO). The color of the solution readily changed to purple. Further, approximately 50 g of solid KOH was added slowly, ensuring that the solution temperature should not rise above 15˚C as it may cause decomposition of Fe(VI). The solution mixture was allowed to cool by standing in a refrigerator for 40 min. The resulting dark purple slurry was filtered with a glass filter (medium porosity 10–15 μm), and the filtrate was discarded. The precipitate was washed with 100 mL of cold/chilled 3 M KOH solution. The filtrate from the washings was collected, taken into a flask and 100 mL of saturated chilled KOH solution was then added. The potassium ferrate readily precipitated, which was filtered again with a GF/C filter. The filtrate was discarded, and the solid was washed with 50 mL of cold 3 M KOH solution, and the filtrate was collected in a beaker. Similarly, re-precipitation was carried out at least 3–4 times to remove any impurities, if present. Finally, the solid was flushed with n-hexane (4×10 mL), dry methanol (2×5 mL) and diethyl ether (2×10 mL). The final product was collected carefully, it was almost black in color and stored in vacuum desiccator. Further, the purity of the product was assessed using UV–visible measurement since the standard molar absorbance of Fe(VI) solution was reported to be $1150\,M^{-1}\,cm^{-1}$ at 510 nm at pH ~ 9.2 [26]. The purity of the synthesized Fe(VI) was found to be >95%.

2.3. UV–visible measurements

Using a UV–visible spectrophotometer (Thermo Electron Corporation, England; Model: UV1), indirectly the degradation of NTA was observed by observing the change in Fe(VI) decomposition. The known concentration of NTA with constant pH (obtained by the phosphate buffer) was taken in a beaker and the known amount of solid Fe(VI) was then added to this solution. Further, the change in absorbance was recorded with time using the UV–visible spectrophotometer at 510 nm. Absorbance of blank solutions, i.e. the Fe(VI) solution (same pH obtained by phosphate buffer) was also recorded simultaneously at 510 nm for necessary absorbance correction. The decrease in absorbance is mainly due to the degradation of NTA in solution. Similar methodology was employed in the degradation of cyanide or other pollutants using Fe(VI) earlier [20,24].

2.4. TOC measurements

Total organic carbon analysis was performed to indicate the degradation level of NTA. Cd(II)–NTA solution (1.0×10^{-4} mol/L) was prepared and a known amount of Fe(VI) was added as to obtain the concentration of Fe(VI) in solution as 1.0×10^{-4} or 2.0×10^{-4} mol/L with constant stirring and at constant pH 10.0 (phosphate buffer). The solutions were stirred constantly maximum for 2 h, and while stirring the aliquots were taken intermittently at different time intervals as to measure the total organic carbon content using TOC analyzer (TOC-5000A, Shimadzu, Japan). The blank solutions were also analyzed for TOC for necessary corrections. Hence, the corrected values inferred to the degradation of NTA in solution.

2.5. Inductively coupled plasma measurements

Similar to the TOC data, the removal of Cd(II) following the degradation of Cd(II)–NTA complex by Fe (VI) was studied by analyzing the total cadmium concentration in the treated solutions using an inductively coupled plasma (Optima 2000 DV, Perkin–Elmer, USA). Cd(II)–NTA complex (1.0×10^{-4} mol/L) was treated with different dosages of Fe(VI) (1.0×10^{-4} mol/L and 2.0×10^{-4} mol/L) and the solutions were constantly stirred in reaction reactors.

The aliquots were taken out at different time intervals, filtered quickly using 0.45 μm syringe filter and subjected to the Cd(II) concentration using ICP. The removal of Cd(II) was calculated as in percentage obtained by using the formula given below:

$$\%\ \text{Removal} = ((C_0 - C_t)/C_0) \times 100$$

where C_0 is the initial concentration of Cd(II) taken and C_t is the concentration of Cd(II) at time "t."

Further, the simultaneous removal of cadmium (*cf.* reaction 5) was observed using the ICP analysis. The Cd(II)–NTA (1.00×10^{-4} mol/L) was treated with two different dosages of Fe(VI), i.e. 1.0×10^{-4} and 2.0×10^{-4} mol/L at constant pH 10.0. Solutions were continuously stirred in the reaction reactor, intermittently the aliquots were withdrawn and filtered with 0.45 μm syringe filter and subjected to the total cadmium analysis using ICP. Results obtained are converted into the percent removal of cadmium and shown in Fig. 5.

2.6. pH dependence study

The 5.0×10^{-4} mol/L of Cd(II)–NTA solution was prepared having the pH of 8, 9, 10, 11 and 12 separately using phosphate buffer and were taken in a reaction reactor. A known amount of Fe(VI) was added in the reactor to achieve the Fe(VI) concentration 1.0×10^{-4} mol/L in solution. The solutions were stirred and the change in absorbance was observed as a function of time. Further, after continuous stirring for ca. 2 h the solutions were filtered using 0.45 μm syringe filter and subjected to its Cd(II) analysis using ICP.

2.7. Kinetics models and data analysis

The studied reduction kinetic data of Fe(VI) by NTA were analyzed in terms of pseudo-first-order and pseudo-second-order sorption equations. In order to obtain rate constants, a linear form of each rate equation was applied. A linear regression line has an equation of the form $Y = a + bX$, where X is the explanatory variable and Y is the dependent variable. The slope of the line is b, and a is the intercept. This experiment was repeated three times and the average values including standard deviations were reported.

3. Results and discussion

3.1. Species of $Fe^{(VI)}O_4^{2-}$ in aqueous solution

Several spectroscopic studies enabled that various protonated and deprotonated species of Fe(VI) are present in solution and these species are predominant at different solution pH, which basically depends on the acidic dissociation constant of that particular species. Fig. 1 depicts the percentage speciation of these species with the function of pH. The speciation was carried out using the known pK_a's values, i.e. $pK_{a1} = 1.6$, $pK_{a2} = 3.5$, and $pK_{a3} = 7.3$ of $Fe^{(VI)}O_4^{2-}$ [14,25]. Fig. 1 clearly indicated that $HFeO_4^-$ and FeO_4^{2-} are predominant in neutral and alkaline pH, in which Fe(VI) was known to be relatively stable towards its spontaneous decomposition to ferric iron, Fe(III) [27]. Fig. 1 also indicated that at pH ~ 10, the only species, i.e. FeO_4^{2-} exists in aqueous solutions.

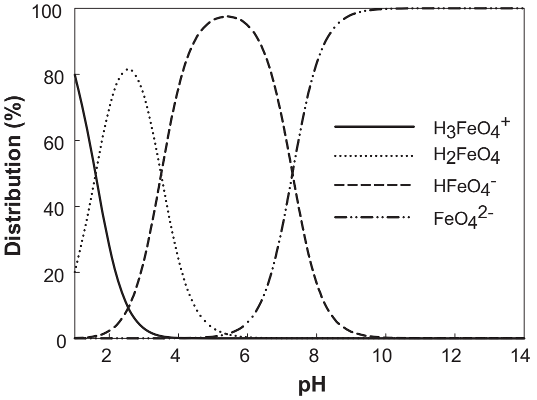

Fig. 1. Speciation of Fe(VI) species in aqueous solutions.

3.2. Degradation of NTA

The UV–visible data recorded at 510 nm were used to analyze the oxidation of NTA at different time intervals. The basic oxidation–reduction reaction involved can be written as (Eq. (1)):

$$\text{NTA} + \text{Fe(VI)} \rightarrow \text{Intermediates} \rightarrow \text{Products} + \text{Fe(III)} \quad (1)$$

The degradation of NTA was primarily observed with the change in Fe(VI) concentration in the solution using UV visible data. Hence, to observe the NTA degradation, various molar ratios of Fe(VI) to NTA were initially taken i.e. 1:0.5–1:15 and the change in absorbance (which is related to the concentration of Fe (VI)) was recorded. Then it was converted to percent reduction of Fe(VI) as shown in Fig. 2. It was noted that increasing the concentration of NTA, a gradual increase of Fe(VI) percentage reduction took place which clearly suggested more decomposition of NTA also took place. Quantitatively, it was noted that increasing the NTA concentration from 5.0×10^{-5} to

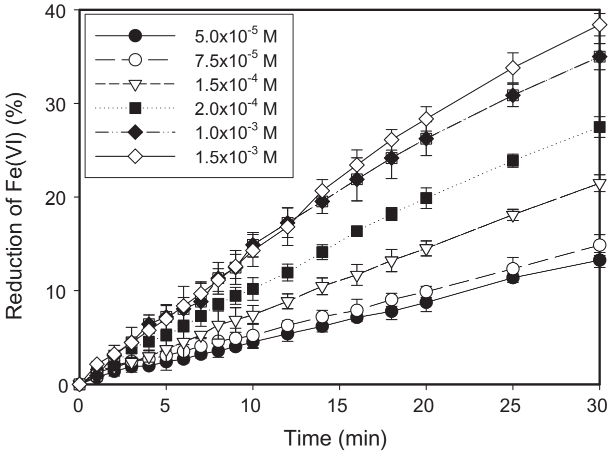

Fig. 2. Reduction of Fe(VI) as a function of time for different concentration of NTA for the constant Fe(VI) concentration 1.0×10^{-4} mol/L at constant pH 10.0.

1.5×10^{-3} mol/L, the respective percent Fe(VI) reduction was increased from 13.3 to 38.4% after 30 min keeping the Fe(VI) concentration at constant, i.e. 1.0×10^{-4} mol/L and solution pH ~ 10.0. Similar results were obtained for the decomposition of CN^- or bisphenol as treated with Fe(VI) in aqueous solutions [24,25].

The rate expression for the reaction of Fe(VI) with NTA can be written as (Eq. (2)):

$$-\frac{d[\mathrm{Fe(VI)}]}{dt} = k \times [\mathrm{Fe(VI)}]^m \times [\mathrm{NTA}]^n \tag{2}$$

where [Fe(VI)] and [NTA] are the concentrations of Fe (VI) and NTA respectively; m and n are their respective order and k is the overall reaction rate constant. Kinetic studies were carried out using the data obtained for the amount of Fe(VI) degraded for various molar ratios of NTA to Fe(VI). Further, Eq. (1) may be written as:

$$-\frac{d[\mathrm{Fe(VI)}]}{dt} = k_1 \times [\mathrm{Fe(VI)}]^m \tag{3}$$

where

$$k_1 = k[\mathrm{NTA}]^n \tag{4}$$

Eq. (3) was used to deduce the rate kinetics in particular to the reduction of Fe(VI). The change in Fe(VI) concentration data obtained individually for different NTA:Fe(VI) molar ratios was used for the first and second-order rate kinetics (as taking $m = 1$ or 2) and was observed that the results were best fitted to the first order rate kinetics (i.e. $m = 1$) since the correlation coefficients (0.988–0.999) were reasonably high comparing to the correlation coefficients (0.894–0.995) obtained for the second order rate constant values (i.e. $m = 2$). Hence, it was assumed that the pseudo-first order rate kinetics was applicable to the decomposition of Fe(VI) in the presence of NTA [23,25,28]. The k_1 values were evaluated for the different molar ratios of the NTA to Fe(VI) and are returned in Fig. 3. It was observed that almost a linear relationship was observed between the k_1 and NTA concentration up to 2×10^{-4} M NTA and then increase of k_1 was much slowed down above 2×10^{-4} M NTA.

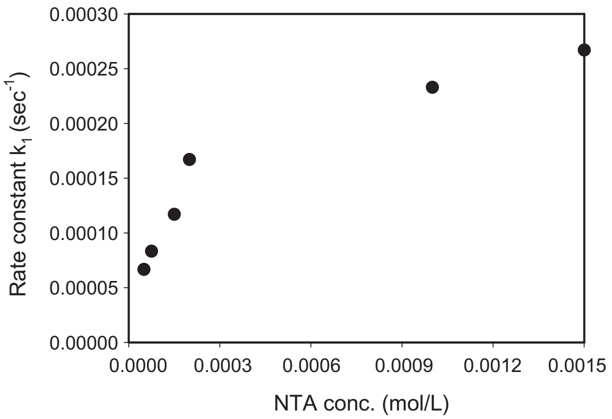

Fig. 3. Variation of k_1 value at different NTA concentration [Fe(VI): 1.0×10^{-4} mol/L; pH 10.0].

3.3. Degradation of NTA in Cd(II)–NTA system

Further, the mixed system of NTA, i.e. Cd(II)–NTA complex was taken and the decomposition of NTA in the Cd(II)–NTA was analyzed using the TOC data. The basic equation may be written as:

$$\begin{aligned}&\mathrm{Fe(VI)} + \mathrm{Cd(II)\text{–}NTA} \rightarrow \text{Decomplexation of}\\&\mathrm{Cd(II)\text{–}NTA} + \mathrm{Fe(III)} \rightarrow \text{Decomposed NTA products}\\&+ \mathrm{Cd(II)} + \mathrm{Fe(III)}\end{aligned} \tag{5}$$

The decomplexation of Cd(II)–NTA was supposed to be a very fast step. However, the decomposition of NTA was noted to be a slow step. The TOC data were collected at various time intervals.

The mixed complex system, i.e. Cd–NTA (1.0×10^{-4} mol/L) was treated with two different dosages of Fe(VI), i.e. 1.0×10^{-4} and 2.0×10^{-4} mol/L keeping the solution pH ~ 10 as constant (phosphate buffer). The TOC values were recorded at different time intervals. Further, based on the TOC values the percent decomposition of NTA was calculated and returned in Fig. 4. Fig. 4 clearly shows that the degradation of NTA increases with increasing the contact time and achieved almost a constant value after the 60 min of contact. Further, maximum 23% of NTA was degraded at the Fe(VI) dosages of 1.0×10^{-4} and 2.0×10^{-4} mol/L. Quantitatively, within 120 min of contact, the TOC values were decreased from 7.01 to 5.40 mg/L (for 1.0×10^{-4} mol/L of Fe(VI) dosages) and 7.01 to 5.40 mg/L (for 2.0×10^{-4} mol/L of Fe(VI) dosages). It was observed that even an increase in Fe (VI) dose, the degradation of NTA was unaffected which inferred that the 1:1 stoichiometry occurred for the NTA to Fe(VI) independent to the Cd(II) presence. Previous results also demonstrated that the stoichiometric ratio obtained between total cyanide and Fe(VI)

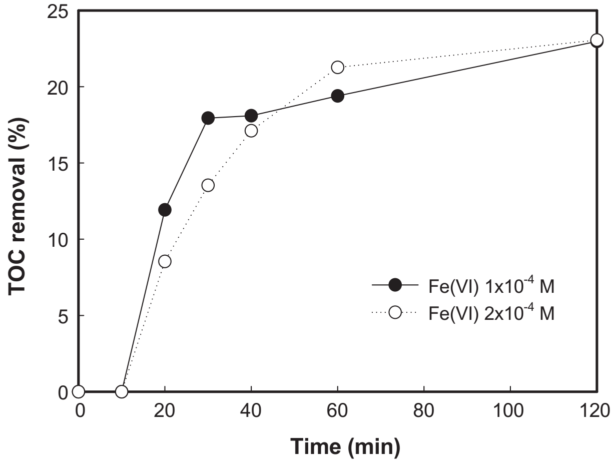

Fig. 4. Percent degradation of NTA in the complexed system of Cd(II)–NTA as a function of time [Cd(II)–NTA: 1.0×10^{-4} mol/L; pH 10.0].

was found to be 1:1 in the degradation of zinc-cyanide complex by Fe(VI) [29].

3.4. Removal of Cd(II) by Fe(VI) as a function of time

Fig. 5 clearly demonstrates that increasing the dosages of Fe(VI) from 1.0×10^{-4} to 2.0×10^{-4} mol/L apparently increased the removal of Cd(II) respectively from 14.9 to 23.8%. Previously, it was observed that maximum of ca. 23% of TOC was removed which was unaffected with the Fe(VI) dose. However, the simultaneous removal of Cd(II) from aqueous solutions was greatly affected with Fe(VI) dose. This increase in percent removal of Cd(II) from aqueous solution may be explicable on the basis that increasing the dose of Fe(VI) caused an increased concentration of Fe(III) in the solution which may enable an enhanced free Cd(II) removal either by the coagulation or adsorption process [30,31].

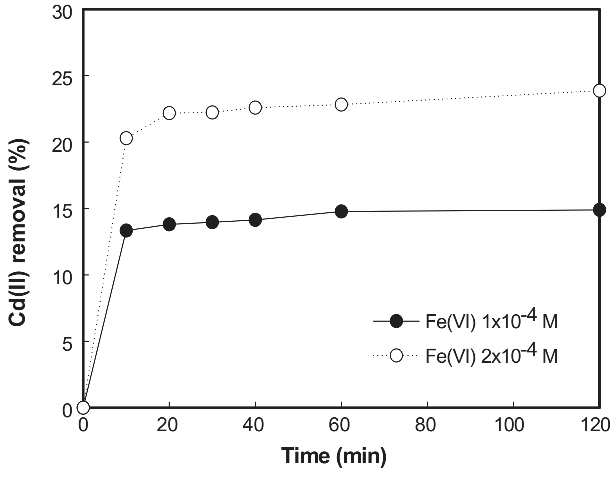

Fig. 5. Percent removal of free cadmium as a function of time for two different dosages of Fe(VI) at pH 10 [Cd(II)–NTA concentration: 1.0×10^{-4} mol/L].

Moreover, it was clearly shown (Fig. 5) that very fast removal of cadmium by Fe(VI) occurred as within few min of contact, maximum cadmium was removed. This indicated that the Fe(VI) which is one of potential coagulant/adsorbent could remove efficiently the free cadmium from aqueous solutions. Previous studies inferred that Fe(VI) could be used in the efficient removal of several cations/anions including Mn^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Cr^{3+}, Hg^{2+}, and As(III) from aqueous solutions via oxidation/coagulation/adsorption process using the lower dose of ferrate(VI), i.e. 10–100 mg/L [32,33]. Additionally, we presumed that at this pH 10.0 the free cadmium is supposed to be precipitated as insoluble $Cd(OH)_2$ and resulted in the decrease in cadmium concentration in the bulk solution.

3.5. Treatment of Cd(II)–NTA complex by Fe(VI) as a function of pH

The pH is an important parameter in the treatment of Cd(II)–NTA complex by Fe(VI). Hence, the study further extended to observe the pH effect (i.e. from pH 8.0–12.0 (using phosphate buffer)) in the treatment of 5.0×10^{-4} mol/L of Cd(II)–NTA solution with 1.0×10^{-4} Fe(VI) dose. The data were collected as the change of percent ferrate reduction as a function of time for different pH condition and are returned in Fig. 6(a). Fig. 6(a) clearly demonstrated that a rapid Fe (VI) reduction was observed at pH 8 in the initial reaction time but much reduced Fe(VI) reduction was noticed at a higher solution pH. This fast increase in Fe(VI) percent decomposition intended that the reactivity of Fe(VI) increases decreasing the pH as at pH 1.0 the redox potential of Fe(VI) was 2.20 V whereas it was reported to be 0.72 V at pH 14 [14–16].

Further, on the other, hand the simultaneous removal of cadmium was obtained at different solution pH and is represented in Fig. 6(b). It was clearly demonstrated that increasing the solution pH from 8.0 to 12.0 could not cause significant change in Cd(II) removal as it was below 5% for all solution pH. This may be explicable with the fact that only five times less Fe(VI) was introduced in the treatment process hence, insignificant of Fe(III) was generated to remove higher concentration of the free Cd(II) from aqueous solutions. Moreover, it was observed that relatively

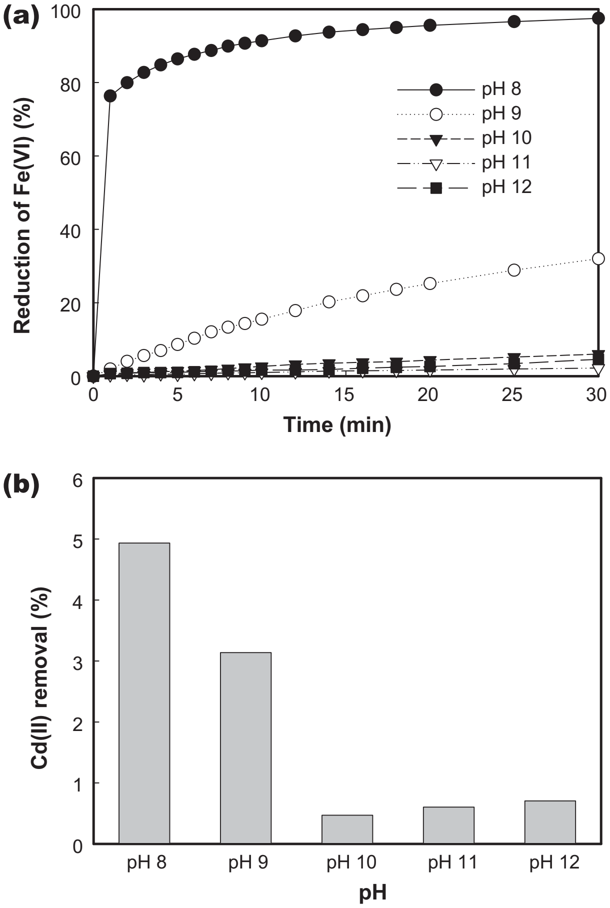

Fig. 6. (a) Reduction of Fe(VI) and (b) removal of Cd(II) as a function of time for different pH (Cd(II)–NTA concentration: 5.0×10^{-4} mol/L and Fe(VI) concentration: 1.0×10^{-4} mol/L).

higher, Cd(II) was removed at low pH, i.e. pH 8.0. This could again confer the results obtained with the Fe(VI) reduction percentage which was obtained relatively higher at lower pH values.

4. Conclusions

The Fe(VI) was prepared by the modified wet oxidation method. Further, the Fe(VI) was used for the degradation of NTA as well the complexed species of Cd(II)–NTA complex systems in an attempt to find cleaner/greener waste water treatment technologies. Fe(VI) was found to be effective for the oxidation of NTA in the single, i.e. NTA and in the complexed system, i.e. Cd(II)–NTA at pH ~ 10. The degradation of NTA in the complexed Cd(II)–NTA system obtained with the TOC data showed that maximum 23% of NTA was degraded. Further, the Fe(VI) converted into Fe(III) as in the form of ferric hydroxide can coagulate/flocculate or even by co precipitation process can remove approximately 23% of free cadmium from the aqueous solutions. pH dependence data obtained in the pH range 8.0–12.0 showed that Fe(VI) found to be more reactive at pH 8.0 than the higher pH values studied at least in the treatment of Cd(II)–NTA. The present study is a useful application of Fe(VI) in the treatment of industrial waste water contaminated with metal complexed species in particular the Cd(II)–NTA species.

Acknowledgments

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