Radiolytic formation of non-toxic Cr(III) from toxic Cr(VI) in formate containing aqueous solutions: A system for water treatment

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ABSTRACT

Toxic hexavalent chromium Cr(VI) in the form of potassium dichromate was radiolytically reduced to non-toxic trivalent chromium Cr(III) in N_2O-saturated aqueous solutions containing formate. This reduction by the electron donor ($CO_2H^{\bullet}/CO_2^{\bullet-}$) produced by continuous radiolysis of water, was a linear function of the absorbed dose. This reaction was pH and dose rate dependent. pH was an important parameter in the reduction, as it affects both chemical speciation of Cr(VI) and formate. Possible mechanisms related to dose rate dependence of removal of Cr(VI) are presented. At pH 3 a decrease in the radiation induced reduction of Cr(VI) was observed with increasing hydrogen peroxide concentration. A mechanism to account for this variation is proposed. These findings suggest that irradiation of Cr(VI) solutions in presence of formate can be effective, economical and simple means for treatment of waste water contaminated with hexavalent Cr(VI).
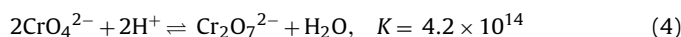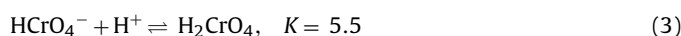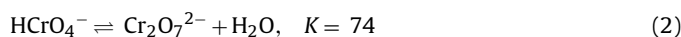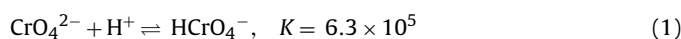
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1. Introduction

Chromium is one of the most toxic metals resulting from numerous industrial activities such as textile dyeing, leather tanning and electroplating [1,2]. The two oxidation states of chromium commonly found in the environment, are trivalent Cr(III) and hexavalent Cr(VI) valence state. The behavior of chromium species depends strongly on their oxidation state: Cr(III) is not carcinogenic and does not bear any toxicological relevance [3]. It is an essential trace element in human nutrition [4]. Chromium(VI) compounds, believed to be the second most common inorganic pollutant after lead [5] are toxic and have been documented to be human carcinogens in a number of studies [6,7]. Being highly mobile, it reaches the groundwater through the waste discharges.

Reduction of Cr(VI) to Cr(III) thus leads to drastic decrease in the toxicity of this element. It is thus essential to remove Cr(VI) from wastewaters before it is discharged into the environment. Numerous studies on the removal of Cr(VI) metal ions from diluted water solutions have been reported in the literature. Strong reducing agents and other metals ions are used to chemically reduce Cr(VI) to Cr(III) [8,9]. In fact these agents and metal ions induce additional environmental problems. Furthermore, various kinds of microorganisms are able to biologically reduce this metal ion [10,11]. However this environmentally friendly practice is limited to the laboratory level and is not efficient at waste sites.

Rivero-Huguet and Marshall [12] found appreciable increases for Cr(VI) reduction rates in the presence of some carboxylic acid (particularly L-cysteine, citric, lactic, malic and tartaric acid), when working at pH ∼ 2. Bae et al. [13] showed that some organic substrates (acetate, citrate, oxalate, lactate, tartrate) slightly stimulated the rate of microbial reduction of Cr(VI). Although many types of electron donors have been selected for removing Cr(VI) from aqueous solution, radiation induced reducing radical $CO_2^{\bullet-}$ (or its protonated form CO_2H^+) obtained from gamma irradiation of Cr(VI) aqueous solution in presence of non-toxic formate has not been investigated to our knowledge.

At its highest oxidation state, +6, hexavalent chromium exists in aqueous solution as several different forms of oxyanions. The most common compounds are the chromate ion CrO_4^{2-}, the hydrogen chromate ion $HCrO_4^-$, the acid chromate H_2CrO_4 and the dichromate ion $Cr_2O_7^{2-}$. All the Cr(VI) forms are linked by a set of equilibria, the relative proportions of which depend on pH and the total Cr(VI) concentration [14,15]:

$$CrO_4^{2-} + H^+ \rightleftharpoons HCrO_4^-, \quad K = 6.3 \times 10^5 \tag{1}$$

$$HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O, \quad K = 74 \tag{2}$$

$$HCrO_4^- + H^+ \rightleftharpoons H_2CrO_4, \quad K = 5.5 \tag{3}$$

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O, \quad K = 4.2 \times 10^{14} \tag{4}$$

At pH < 1, the predominant species is H_2CrO_4. At pH > 8 only the chromate ion CrO_4^{2-} exists. At pH ranging from 2 to 6, the hydrogen chromate $HCrO_4^-$ and the dichromate $Cr_2O_7^{2-}$ anions prevail.

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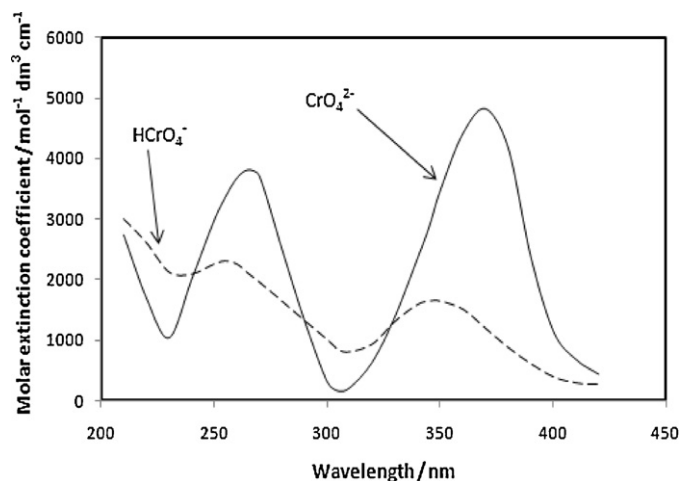
Fig. 1. Absorption spectra of 6×10^{-4} M Cr(VI) solution: (—-) pH 3, (––––) pH 9.2.

In the present work, Cr(VI) was always obtained from potassium dichromate $K_2Cr_2O_7$. It is expected from the value of the dimerization constant of $HCrO_4^-$ (equilibrium (2)) that when $Cr_2O_7^{2-}$ concentration is less than 10^{-3} mol dm^{-3}, as the case in this work, more than 96% of the Cr(VI) exists in the monomeric form $HCrO_4^-$. Therefore the dimerization of Cr(VI) does nearly not occur and need not to be taken into account.

Fig. 1 shows the optical absorption spectra of the oxyanions $HCrO_4^-$ and CrO_4^{2-} present in dilute solutions.

One of the techniques implemented recently is the use of ionizing radiation for industrial wastewater treatment. There are many types of ionizing radiations such as gamma and X-rays, beta and alpha particles. However, high energy electrons [16,17] and gamma radiation from either ^{60}Co or ^{137}Cs [18] are mostly used due to their high penetrating power.

The method is based on radiation-induced chemical reduction of the metal ions to their respective metals or to lower oxidation state ions. The objectives of this study were to evaluate the removal of the toxic hexavalent chromium by irradiating the solution with γ-irradiation in the presence of formate as hydroxyl radical scavenger. We also investigated the effect of the concentration of formate, the pH of the medium and the dose rate on this removal.

2. Experimental

2.1. Chemicals

All solutions were prepared with triply distilled water, purified and deionized by a Millipore Milli-Q system. All the reagents used in this work were Analar grade from BDH and were used as received. The pH of solutions (measured with E.I.L. 7020 glass electrode calibrated with pH 4 and pH 9.2 buffers before use) was adjusted when necessary using perchloric acid or sodium hydroxide. The average chromium concentration in wastewater is comparable to that used in this work [19].

2.2. Sample preparation and irradiation

20 cm^3 of the solution was pipetted into an air tight tube sealed with a rubber stopper and equipped with a 10 mm spectrophotometer cell on a side arm. All the solutions prior to irradiation were saturated with high purity nitrous oxide, by bubbling the pure gas for about 30 min prior to irradiation. Steady state irradiations were carried out at room temperature using a ^{60}Co γ-ray source (2000 Ci nominal activity). Different dose rates were obtained by irradiating the solution at known distances from the source. Doses were

Table 1
G-values of some water radiolysis species [23].

Species	G-value at 25 °C (in µmol J^{-1})
H_2	0.047
H_2O_2	0.070
e_{aq}^-	0.270
$H^\bullet$	0.070
$OH^\bullet$	0.270
H^+	0.027
OH^-	0.044

measured with Fricke dosimeter [20]. The total dose was varied by changing the irradiation duration. The irradiation was interrupted periodically in order to allow the absorption spectrum of the solution to be measured.

2.3. Analysis of the steady state products

Decay of Cr(VI) was analyzed using its optical absorption. All spectrophotometric analyses were carried out in the γ-irradiation cell using a UV–vis double beam spectrophotometer (Pye Unicam SP8-100) at room temperature, using 2 nm bandwidth.

2.4. Measuring of the reduction of Cr(VI)

The radiation chemical yield for the reduction of Cr(VI), expressed in terms of G-value, is the number of moles of species changed for each joule of absorbed energy (µmol J^{-1}) and is given by:

$$G(-Cr(VI)) = \frac{S}{\varepsilon l \rho} \tag{1'}$$

where ε is the molar extinction coefficient (Fig. 1) of $HCrO_4^-$ (161 m^2 mol^{-1} at 350 nm) or CrO_4^{2-} (481 m^2 mol^{-1} at 370 nm), l is the cell optical path length in cm, ρ is the density of the aqueous solution (1 kg/dm^3) and S is the slope of the linear relationship absorbance of Cr(VI) versus dose in Gy^{-1}.

3. Results and discussion

Within 10^{-9} s the direct ionization and excitation of water molecules in aqueous solutions by radiation like photons or high energy electron beam results in the formation among others of two transient reducing radicals: solvated electron (e_{aq}^-) and hydrogen atom ($H^\bullet$); one oxidizing radical: hydroxyl $OH^\bullet$ and molecular products: hydrogen peroxide H_2O_2 and hydrogen H_2 along the irradiation track [21]:(5)$H_2O \rightsquigarrow e_{aq}^-$, $OH^\bullet$, $H_2^\bullet$, H_2O_2, H^+, OH^-

These primary radiolytic species are produced close to one another in "spurs" and some react with each other very quickly by spur reactions [22]. Radical–radical reactions will generally be of much less significance, compared with radical–solute reactions, in γ-radiolysis studies where the dose rates, are of lower magnitude. Table 1 shows the typical G-values of these primary species at pH 7 applicable to dilute aqueous solutions when all the spur reactions are complete, i.e. about 100 ns after the initial event of deposition of energy in the system [23].

In all cases, unless otherwise stated the concentration of Cr(VI) used in this work was 4×10^{-4} mol dm^{-3}. N$_2$O gas scavenges the hydrated electrons to produce the O$^-$ anions as in the following reaction [24]:
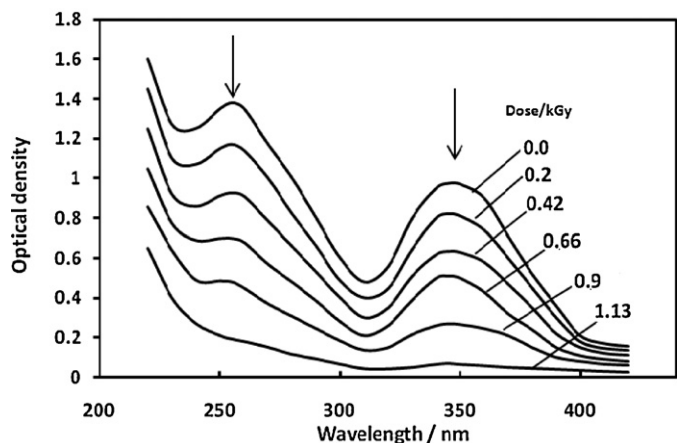
$$e_{aq}^- + N_2O \rightarrow O^- + N_2 \tag{6}$$
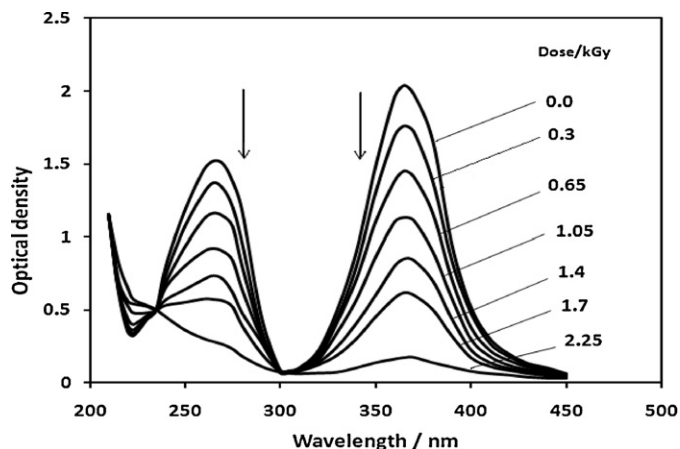
followed by

$$O^- + H_2O \rightarrow OH^\bullet + OH^- \tag{7}$$

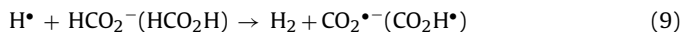**Fig. 2.** Radiation induced bleaching of the $HCrO_4^-$ absorption spectrum pH 3 N_2O saturated solution containing 6×10^{-4} mol dm^{-3} of $HCrO_4^-$ and 10^{-2} mol dm^{-3} of HCO_2^-, dose rate 22.4 Gy min^{-1}.

which converts the atomic oxygen anion O^- into the oxidizing hydroxyl radical $OH^\bullet$. To inhibit $OH^\bullet$ reactions with radiolytically produced Cr(V), Cr(IV) and Cr(III), formate (HCO_2^-/HCO_2H) with its simple one-carbon molecular structure was used as $OH^\bullet$ and $H^\bullet$ scavenger since it is known to react efficiently with these two free radicals by hydrogen abstraction [25]. The following reactions take place:

$$OH^\bullet + HCO_2^-(HCO_2H) \rightarrow H_2O + CO_2^{\bullet-}(CO_2H^\bullet) \quad (8)$$

$$H^\bullet + HCO_2^-(HCO_2H) \rightarrow H_2 + CO_2^{\bullet-}(CO_2H^\bullet) \quad (9)$$

The pK_a for $CO_2H^\bullet/CO_2^{\bullet-}$ was found to be 1.4 [25] and most recently 2.3 [26]. Therefore the carboxyl anion $CO_2^{\bullet-}$, known as an excellent reducing radical [27,28], is the main reducing species for Cr(VI) over our experimental range of $[H^+]$. The overall stoichiometry of the reduction of Cr(VI) is given by:

$$Cr(VI) + 3CO_2^{\bullet-} \rightarrow Cr(III) + 3CO_2 \quad (10)$$

converting toxic Cr(VI) into non toxic Cr(III). It should be noted that subsequent solid phase precipitation, formation of atomic chromium (Cr^0) was not observed. Chromium(III) aquo-complexes are known to be kinetically stable and react very slowly with reducing agents [29].

3.1. Removal of Cr(VI)

Figs. 2 and 3 show the radiation induced bleaching of Cr(VI) in the N_2O-saturated acid solution containing 6×10^{-4} mol dm^{-3} of $HCrO_4^-$ and 10^{-2} mol dm^{-3} of HCO_2^- at pH 3 and pH 9.2 respectively. It should be noticed that no wavelength shift in the peaks of absorption was observed for both pHs.

This radiation-induced removal of Cr(VI) is a linear function of the absorbed dose (Figs. 4 and 5). Cr(VI) removal factor (% R) was calculated from Eq. (2):

$$\%R = \frac{C_a}{C_0} \times 100 \quad (2')$$

where, C_a is the amount of removed metal ion at time t in mol dm^{-3} calculated as the difference in Cr(VI) concentration in the aqueous solution before and after an irradiation time t, C_0 is the initial concentration of Cr(VI) in mol dm^{-3}. To avoid any discrepancy in experimental results, all the measurements were made triplicate with a reproducibility margin on the order of 1%.

The kinetics of the radiation induced reduction of Cr(VI) in presence of formate was investigated at pH 3 and pH 9.2 (Figs. 4 and 5) respectively). At pH 3 the rate of removal obtained by using the
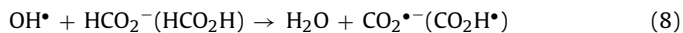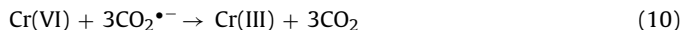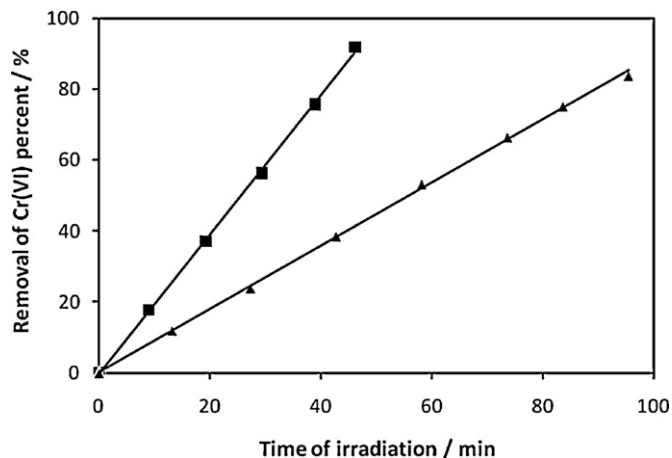

Fig. 3. Radiation induced bleaching of the $HCrO_4^-$ absorption spectrum pH 9.2, N_2O saturated solution containing 4×10^{-4} mol dm^{-3} of $HCrO_4^-$ and 10^{-2} mol dm^{-3} of HCO_2^-, dose rate 22.4 Gy min^{-1}.

Fig. 4. Removal percentage of Cr(VI) vs time of irradiation. (■) pH 3 and (▲) pH 9.2 of 6×10^{-4} mol dm^{-3} of $HCrO_4^-$ and 10^{-2} mol dm^{-3} of HCO_2^-, dose rate: 22.4 Gy min^{-1}.

slope of linear least square regression line of the removal percentage versus the corresponding time intervals is approximately 2% min^{-1}. Increasing pH to 9.2 decreased the removal rate of Cr(VI) to approximately 0.9%.
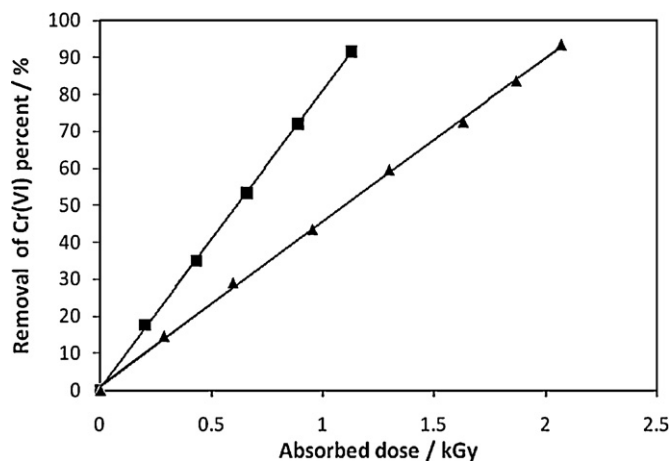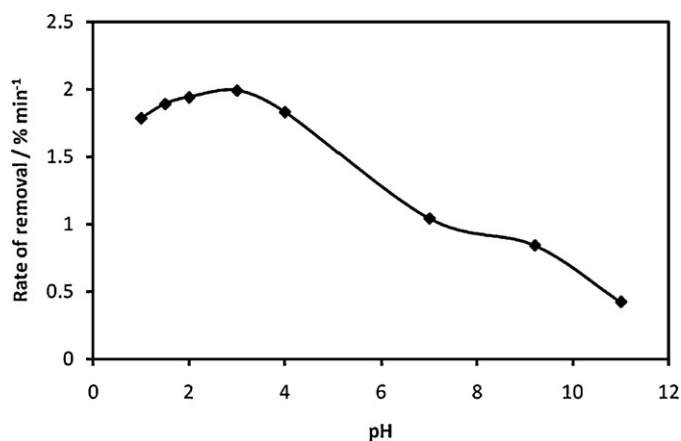

Fig. 5. Dependence of Cr(VI) removal vs time of irradiation under different absorbed doses. (■) pH 3 and (▲) pH 9.2 of 6×10^{-4} mol dm^{-3} of $HCrO_4^-$ and 10^{-2} mol dm^{-3} of HCO_2^-, dose rate: 22.4 Gy min^{-1}.

Fig. 6. Effect of pH on G($-$Cr(VI)) in N_2O-saturated solution of 4×10^{-4} mol dm^{-3} of Cr(VI) and 10^{-2} mol dm^{-3} of HCO$_2^-$. Dose rate: 22.6 Gy min^{-1}.

3.2. Effect of the pH on the reduction of Cr(VI)

Reduction of Cr(VI) by formate has been investigated in solutions at different pH values. Solutions saturated with N_2O and containing 4×10^{-4} mol dm^{-3} of Cr(VI) and 10^{-2} mol dm^{-3} of formate were γ-irradiated at pH's ranging from 1 to 11.2. A plot of G($-$Cr(VI)) versus pH is shown in Fig. 6. An optimum Cr(VI) reduction occurs around pH 3. Such dependence was also observed in other studies where it has been found that low (∼4) and intermediate pH (∼7) favor the reduction of Cr(VI) but at high pH (∼9), the production of Cr(III) is greatly decreased [30]. The low reduction yield at higher pH was also reported later [31–34]. In order to account for the increase in the rate of removal of Cr(VI) with decreasing pH, one needs to consider the speciation of both Cr(VI) and carbon dioxide radical anion in the pH range studied here. Cr(VI), as HCrO$_4^-$, shows a high redox potential (+1.33 V) in acidic conditions and noticeably lower redox potential, as CrO$_4^{2-}$, (−0.12 V) under more basic conditions [35]. Furthermore the redox potential for the couple CO$_2$•$^-$/CO$_2$ is reported to be −1.98 V [36] and between −1.98 and −1.1 V by [37]. CO$_2$•$^-$ can easily reduce HCrO$_4^-$ than CrO$_4^{2-}$. Consequently electron transfer from CO$_2$•$^-$ to CrO$_4^{2-}$ is energetically less favored than from CO$_2$•$^-$ to HCrO$_4^-$.

Another explanation is that formate reduces the intermediate state Cr(IV) at low pH and not at high pH due to the difference in reactivity between the undissociated (CO$_2$H•) and dissociated forms of formate (CO$_2$•$^-$) toward the intermediate Cr(IV) state [38].

3.3. Effect of the dose rate and formate concentration on Cr(VI) removal

Under high dose rate condition, the rate of production of radicals is high but the probability of interradical reactions (OH• + OH• → H$_2$O$_2$, H• + H• → H$_2$ and H• + OH• → H$_2$O) increases within the spurs [39]. The loss of OH• and H• radicals leads to the decrease of the yield of removal of Cr(VI) as illustrated in Fig. 7. Table 2 gives the decrease in the rate of removal as a function of formate concentration in the dose rate range 0.3–32.5 Gy min^{-1}.

Table 2
Decrease in the rate of removal as a function of formate concentration in the dose rate range [0.3–32.5] Gy min^{-1}.

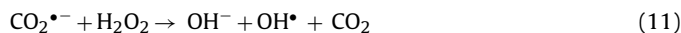| [HCO$_2^-$] (mol dm^{-3})	Decrease in the rate of Cr(VI) removal (in %)
10^{-4}	20
10^{-3}	23
10^{-2}	40
10^{-1}	45
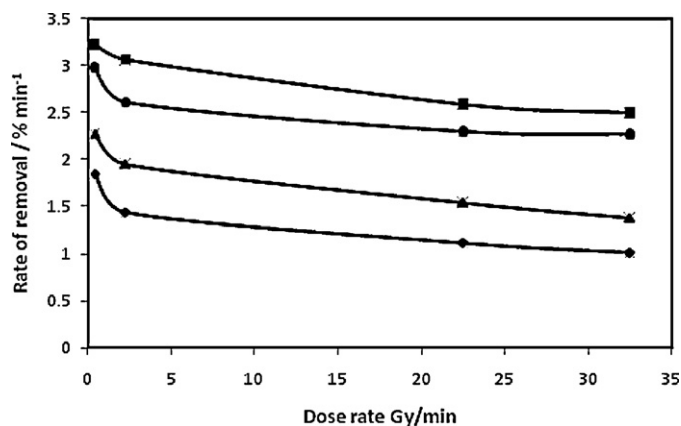
Fig. 7. Variation of the rate of removal of Cr(VI) as function of dose rate and [HCO$_2^-$] in N_2O saturated solution, pH 3. [HCrO$_4^-$] = 4×10^{-4} mol dm^{-3}, N_2O saturated solution, pH 3. [HCO$_2^-$]: (■) 10^{-1} mol dm^{-3}, (●) 10^{-2} mol dm^{-3}, (▲) 10^{-3} mol dm^{-3}, (♦) 10^{-4} mol dm^{-3}.

3.4. Effect of hydrogen peroxide

The decomposition of hydrogen peroxide by Cr(VI) species has been studied over a wide range of pH. H$_2$O$_2$ acts as a oxidizing agent for Cr(III) in Fenton-type reaction at pH > 7.5 [40,41] and as a reducing agent for Cr(VI) at lower pH [42]. Yet we have noticed that the kinetics of this reduction depends on the hydrogen ion concentration. At pH 3, the change of the optical density at 350 nm of the 1.2 mmol dm^{-3} Cr(VI)–0.7 mmol dm^{-3} H$_2$O$_2$ solution was slow (2% of Cr(VI) disappears after 1 h).

When initially added, the hydrogen peroxide reacts with formate according to:

$$CO_2\text{•}^- + H_2O_2 \rightarrow OH^- + OH\text{•} + CO_2 \tag{11}$$

followed by

$$OH\text{•} + HCO_2^- \rightarrow H_2O + CO_2\text{•}^- \tag{12}$$

CO$_2$•$^-$ is then consumed, leading to a net decrease in the yield of reduction of Cr(VI) with increased added [H$_2$O$_2$] as shown in Fig. 8. When all the formate is consumed (either by HCrO$_4^-$ or by H$_2$O$_2$), HCrO$_4^-$ recovers with the same G-value (0.125 μmol J^{-1}) whatever the initially added H$_2$O$_2$ concentration was.

However in the pH range 0.5–1.5, a fast drop was seen in the optical density suggesting that the chromic acid H$_2$CrO$_4$ species,
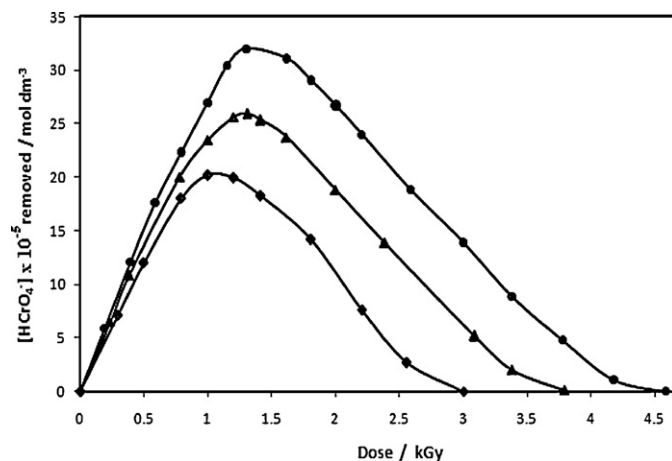
Fig. 8. Effect of hydrogen peroxide on the reduction yield of Cr(VI) in pH 3 N_2O saturated solution. 0.4 mmol dm^{-3} of HCrO$_4^-$, 1 mmol dm^{-3} of HCO$_2^-$. Dose rate 32.5 Gy min^{-1}. (●) [H$_2$O$_2$] = 0, (■) [H$_2$O$_2$] = 0.5 mmol dm^{-3}, (▲) [H$_2$O$_2$] = 0.15 mmol dm^{-3}.
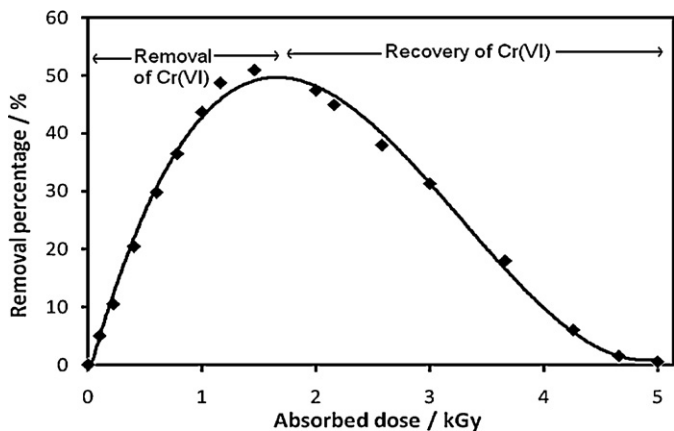
Fig. 9. Recovery of Cr(VI) in N_2O-saturated solution of $[HCrO_4^-] = 4\,mmol\,dm^{-3}$, $[HCO_2^-] = 1\,mmol\,dm^{-3}$, dose rate; $32.5\,Gy\,min^{-1}$, pH 3.

which is predominant at this pH range, reacts sufficiently fast with the hydrogen peroxide to give the peroxochromium(VI) complex [43] called blue perchromic acid, according to the stoichiometry:

$$2H_2CrO_4 + 6H^+ + 3H_2O_2 \rightarrow 2Cr^{3+} + 3O_2 + 8H_2O \tag{13}$$
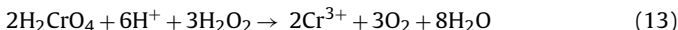
3.5. Recovery of Cr(VI)

Complete recovery of Cr(VI) is seen after all the $HCO_2^{\bullet-}$ has been consumed in pH $3\,N_2O$-saturated solutions. In this case, e_{aq}^- are converted to oxidizing species $OH^\bullet$, which oxidize Cr(III) back to Cr(VI). In this case $G(\text{oxidizing species}) = G(e_{aq}^-) + G(OH^\bullet) > G(\text{reducing species}) = G(H^\bullet)$.

$$Cr(VI) + 3H^\bullet \rightarrow Cr(III) + 3H^+ \tag{14}$$

$$Cr(III) + 3OH^\bullet \rightarrow Cr(VI) + 3OH^- \tag{15}$$
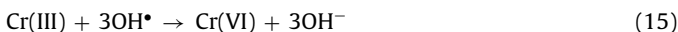
The net result between these two competing reactions leads to the recovery of Cr(VI) from the stable Cr(III) as shown in Fig. 9, where Cr(VI) smoothly recovers after 1.6 kGy when all the formate was used up.

4. Conclusion

In this laboratory-scale study we investigated the feasibility of using the gamma irradiation technique to develop a new method in a global integrated approach for the removal of toxic Cr(VI) present as a major pollutant in industrial wastewater.

The following conclusions have been drawn:

- The amount of Cr(VI) ions removed increased proportionally with the absorbed dose.
- The removal of hexavalent chromium ion is accelerated by addition of formate to the solution.
- The removal was highly dependent on pH. Results indicated that the maximum removal rate was obtained at pH 3 (at a rate of approximately $2\%\,min^{-1}$).
- Recovery of Cr(VI) following oxidation of Cr(III) occurs when all the formate was reacted.

However this laboratory-scale study should be further tested in the field using a pilot plant where successive stages progressively remove contaminants from raw wastewater. This radiation process might be integrated in the multistage water treatment process.

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