Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20503

71 (2017) 136–144
April

Removal of heavy metal ions from wastewater samples using electron beam radiation in the presence of TiO_2

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Received 3 September 2016; Accepted 13 January 2017

ABSTRACT

Removal of heavy metals from wastewater samples through the application of electron beam (EB) radiation in the presence of formate ion as the hydroxyl radical scavenger, and TiO_2 nanopowder as the adsorbent and/or photocatalyst is proposed. The effect of some experimental parameters, such as radiation dose of EB, amount of TiO_2 and solution initial pH, on the removal efficiency of Cd(II), Pb(II) and Cr(VI) metal ions was studied. Aqueous solutions of metal ions with pH value of 7.0 were irradiated by EB in the presence and absence of TiO_2. The obtained results revealed that the removal efficiencies of Cd(II), Pb(II) and Cr(VI) ions were 71.0% (±2.6%), 84.0% (±2.3%) and 83.0% (±1.5%), respectively, by applying 6 kGy dose in the absence of TiO_2. The addition of 0.9 g L^{-1} TiO_2 to the metal ions solutions showed an enhancement in the removal efficiencies (96.0% (±3.8%), 99.1% (±2.7%) and 94.0% (±1.8%), respectively) with the same (6 kGy) radiation dose. Furthermore, it was observed that the required radiation dose to achieve the similar removal efficiencies decreased to 3 kGy in the presence of TiO_2, indicating the synergistic effect through the combination of EB and TiO_2. Finally, the method was applied to the oil refinery and the paint industrial effluents as the real wastewater sources, successfully.

Keywords: Heavy metals; Electron beam; TiO_2; Wastewater

1. Introduction

Nowadays heavy metal ions are among the most important pollutants in surface waters and groundwaters [1]. The major source of the metallic pollutants in the aquatic systems is the discharge of untreated industrial effluents by various industries such as oil refinery, as well as paint manufactures etc. Industrial wastewaters containing lead, cadmium, chromium etc. can contaminate the groundwater resources leading to health and environmental problems [2]. Therefore, removal of the toxic heavy metals from the effluents is necessary prior to the release into the environment. Several methods including chemical precipitation [3], reverse osmosis [4], ion exchange [5], membrane filtration [6], coagulation [7], solvent extraction [8], adsorption [9] and electrochemical treatment techniques [10] have been employed in order to eliminate the heavy metal ions from wastewater. Although the aforementioned techniques can all be used for the removal of heavy metals up to some extent, access to some treatment techniques that can reduce these pollutants to quite low concentrations seems to be an undeniable demand.

A wide variety of organic and inorganic toxic chemicals at low concentrations are noted to be effectively removed by some heterogeneous photocatalysts including TiO_2 [11]. In this method, under the light of energy higher than the semiconductor's bandgap (Eg), the electron–hole pairs were formed in the conduction and valence bands (VB) of the semiconductor, respectively. These charge carriers, which

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migrate toward the semiconductor's surface, are capable of reducing or oxidizing the pollutant species having suitable redox potentials. Despite its advantages, since in this technique, the chemical reactions occur only on the surface of photocatalyst; the species of interest must be carried through the catalyst surface. Moreover, the short penetration of ultraviolet (UV) radiation into the photocatalyst inhibits the utilization of a large reactor. TiO_2 is a poor visible light absorber, hence requiring a large bandgap energy (Eg = 3.2 eV) for the excitation of electrons from the filled VB to the vacant conduction band (CB). In order to enhance the photoresponse and the photoactivity of TiO_2, a variety of approaches have been employed including high energy electron beam (EB) irradiation of TiO_2 [12]. However, there was a small blueshift in the case of TiO_2 samples irradiated by EB, since the EB irradiation might result in a slight reduction in particle size [13]. The decrease in particle size has an obvious effect, i.e., increases the surface energy, which can be attributed to the quantum size effect [14]. The bandgap obtained for the irradiated TiO_2 samples were larger than that of original TiO_2. This increase of bandgap might occur due to size reduction of the semiconductor caused by EB [13]. Furthermore, the formation of active sites on the surface of the catalyst by EB radiation contributes to photocatalytic efficiency [14].

In competition with the existing technologies, ionizing radiations such as gamma rays and EBs were also studied as the clean and promising technology for the removal of heavy metal ions from the aqueous solutions [15–17]. This method is based on the radiation–chemical reduction of the metal ions to their respective elements or to lower oxidation state ions, which can be removed by filtration. Although the removal of heavy metals from water through ionizing radiation has already been studied, to the best of our knowledge, the removal of Cd(II), Pb(II) and Cr(VI) ions from the solutions containing TiO_2 induced by EB has not been explored yet. In continuation to our previous report on application of EB radiation [18], in the present study, aqueous heavy metal solutions were irradiated with EB in the presence and absence of TiO_2, and the effect of TiO_2 amount on the removal efficiency was investigated.

2. Material and methods

2.1. Chemicals and reagents

The metal salts, $PbCl_2$, $CdCl_2.2H_2O$ and $K_2Cr_2O_7$, and other chemicals with highest available purity were obtained from Merck Company (Darmstadt, Germany). TiO_2 (P25) nanopowder with a primary particle size of 21 nm, a crystal structure of mainly anatase (80% by weight) and a specific surface area of 50 $m^2\ g^{-1}$ was purchased from Degussa Company (Essen, Germany). Stock solutions of the metal ions 10 mg L^{-1} were prepared in distilled–deionized water. Sodium formate solution (10^{-2} mol L^{-1}) was prepared as the hydroxyl radical scavenger. Experimental solutions with desired concentrations were obtained through successive dilutions of stock solutions with distilled water. The pH of solutions was adjusted with 0.1 mol L^{-1} HCl and/or NaOH solutions. 1,5–Diphenyl carbazide solution of 1 %w/v was prepared in ethanol as the spectrophotometric reagent for determination of Cr(VI).

2.2. Apparatus

EB irradiation was performed with a 10-MeV accelerator (Rhodotron TT200, Belgium) calibrated with FWT-60 film dosimeter to measure the absorbed dose.

A digitally calibrated pH/ion-meter Metrohm, model 827 (Herisau, Switzerland) furnished with a combined glass–calomel electrode was used to measure/adjust the solution pH.

The concentrations of the metal ions Cd(II), Pb(II) and total Cr (i.e., (III) and (VI)) were determined by a Buck Scientific atomic absorption spectrometer model 210 (VGP, USA), equipped with a deuterium lamp background corrector. Hollow cathode lamps of lead, cadmium and chromium operating at 217.0, 228.8 and 357.9 nm, respectively, were used as the light sources. The lamp currents and slit widths of monochromator were set at 15, 4, and 10 mA; and 0.3, 0.7, and 0.1 nm, respectively. Air-acetylene flame was used for all the measurements. The analysis of Cr(VI) was carried out by colorimetric method using a PerkinElmer, Lambda 25 UV–Vis spectrophotometer (Waltham, MA, USA). Magnetic stirrer, Heidolph model MR3001K (Schwabach, Germany), was used for agitation of the phases and dispersion of TiO_2 particles. A JULABO model MP5 circulating thermostatic water bath (Seelbach, Germany) was used for temperature control during the experiments.

2.3. Experimental method

20 mL aliquots of each metal ion solution containing 10 mg L^{-1} Cd(II), Pb(II) and Cr(VI) were transferred to Petri dishes; 3 mL of 10^{-2} mol L^{-1} sodium formate solution was added to the samples as the hydroxyl radical scavenger; and the pH was adjusted at 7.0. The solutions were deaerated by purging N_2 gas for 15–20 min, and then irradiated immediately at a velocity of 16.6 cm s^{-1} (absorbed dose of 6 kGy). In the second part of the experiments, TiO_2 nanopowder was added to the metal ions solutions. The solutions were covered by aluminum foil and deaerated by N_2 gas through the inlet and outlet silicon tubes tightly fitted into the foil. To disperse/disaggregate TiO_2 particles, the solutions were stirred magnetically for 2 h under the N_2 gas flow (10 mL min^{-1}), and then irradiated at a velocity of 33.2 cm s^{-1} (i.e., 3 kGy absorbed dose). The precipitates formed upon the irradiation, along with the metal ion-loaded TiO_2, were separated from solution by centrifuging at 5,000 rpm for 5 min. Then the changes in concentrations of (Cd(II), Pb(II) and total Cr) ions were determined by flame atomic absorption spectrometer, and that of Cr(VI) by UV–Vis spectrophotometer (using 1,5-diphenylcarbazide method at $\lambda = 540$ nm) [19] in the treated and untreated samples. The removal efficiencies were calculated from the ratio of the results obtained (before and after treatment) by Eq. (1):

$$\%\text{Removal} = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

where C_i and C_f are the concentrations of metal ions before and after treatment, respectively.

3. Results and discussion

In order to estimate the possibility of any photochemical reaction occurrence in the absence of TiO_2 and EB, blank experiments were carried out. The experiments were performed under identical conditions for all metal ions with initial concentration of 10 mg L^{-1}. It was observed that no reduction of Cd(II), Pb(II) and Cr(VI) contents took place during the 2 h of mixing. In this study, no attempt was made to adjust the pH of the solutions, and experiments were carried out in natural pH for physical adsorption of the metal ions except for Cr(VI), where the pH was adjusted to 4.0 by dilute HCl solution. The results demonstrated no observable variation in metals concentrations, so it can be concluded that no adsorption occurs on the glass plate.

3.1. Elimination of metal ions by EB irradiation in the absence of TiO_2

Irradiation of water by EB leads to the production of both reducing and oxidizing species according to the following equation (Eq. (2)) [20]:

$$H_2O \xrightarrow{EB} e^-_{aq}(0.26) + H^{\cdot}(0.06) + OH^{\cdot}(0.27) \\ + H_2(0.04) + H_2O_2(0.07) + H^+(0.27) \quad (2)$$

The radiation chemical yields (*G* values in brackets) of the primary species in water radiolysis indicate that the hydroxyl radical ($OH^{\cdot}$), hydrated electron (e^-_{aq}) and hydrogen atom ($H^{\cdot}$) are the most reactive species. Hydrated electron and H atoms can reduce heavy metal ions while the hydroxyl radicals oxidize them. To exclude the negative impact of hydroxyl radicals, some scavengers such as formate ions are generally used to convert them into reducing species. In the presence of formate ions, OH radicals (and H atoms) are converted to COO^- radical ions, which reduce the metal ions and produce CO_2 by-product [21].

To examine the effect of formate ion on the removal efficiency, laboratory-made water samples containing 10 mg L^{-1} of Cd(II), Pb(II) and Cr(VI) ions were initially prepared with and without adding formate ions. Then all the samples were irradiated by the EB with 1, 3, 6 and 9 kGy doses. As shown in Fig. 1, in the absence of formate ions, the removal efficiencies of Cd(II), Pb(II) and Cr(VI) metal ions were less than 10.5% for all the applied doses, indicating the existence of competitive oxidative reaction as result of the metal ion reactions with OH and H_2O_2 species [21]. Nevertheless, the removal efficiencies from the solutions containing formate ions (1.3×10^{-3} mol L^{-1}) increased significantly with all radiation doses. For instance, the removal efficiencies of Cd(II), Pb(II) and Cr(VI) metal ions were obtained as 51.7% (±2.5%), 66.0% (±3.7%) and 68.0% (±3.6%), respectively, when irradiated with 1 kGy dose. With the augmentation of the irradiation doses from 1 to 6 kGy, these values further increased to 71.9% (±1.5%), 84.6% (±2.3%) and 86.0% (±2.6%), respectively.

However, as illustrated, no significant changes were observed in the removal efficiencies by irradiation at 9 kGy dose, indicating that 6 kGy can be applied as the optimum dose in the removal process. The removal of metal ions from the solutions was due to their reaction with the reducing products of water radiolysis (e^- and H atoms), which led to the formation of lower oxidation state ions and/or metallic Cd, Pb and Cr, that can be removed by filtration. The increase in the removal efficiency with increasing radiation dose was due to the generation of more reducing species. The reduction process suggested by Pikaev [21] is the result of reaction of metal ions with reducing products of water radiolysis (e_{aq} and H atoms). For instance the reduction mechanism for Cd can be written as:

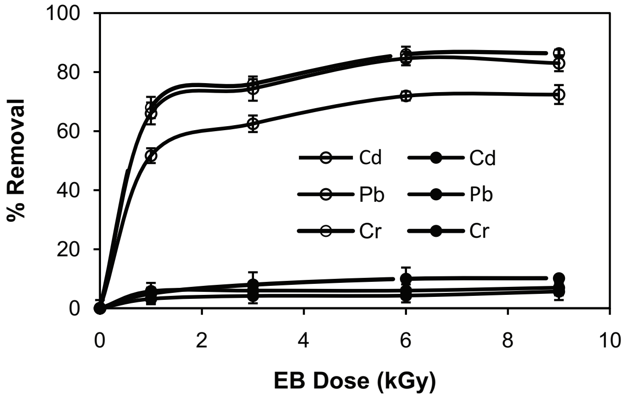

Fig. 1. Effect (absence (●) and presence (○)) of formate ions on the removal efficiencies of Cd(II), Pb(II) and Cr(VI) ions irradiated with different doses of EB (conditions: sample volume – 20 mL; concentration of each metal ion – 10 mg L^{-1}; pH – 7.0).

$$Cd(II) + e_{aq} \rightarrow Cd(I) \quad (3)$$

$$Cd(II) + H \rightarrow Cd(I) \quad (4)$$

$$Cd(I) + Cd(I) \rightarrow Cd(0) + Cd(II) \quad (5)$$

$$nCd(0) \rightarrow Cd(0)_n \quad (6)$$

However, Cd(I) ions not only participate in reaction in Eq. (5) but also are oxidized by OH radicals and hydrogen peroxide (the water radiolysis products) and H_2O_2 formed in reactions of e_{aq} and H atoms with oxygen present in the system as follows:

$$Cd(I) + OH \rightarrow Cd(II) + OH^- \quad (7)$$

$$Cd(I) + H_2O_2 \rightarrow Cd(II) + OH + OH^- \quad (8)$$

$$Cd(I) + H_2O + H^{\cdot} \rightarrow Cd(II) + H_2O_2 \quad (9)$$

To suppress the reactions in Eqs. (7)–(9), two requirements are necessary: (i) the absence of oxygen in the water and (ii) the presence of a scavenger of OH radicals (e.g., formate ions). As noted earlier in the presence of formate ions, OH radicals (and H atoms) are converted to $^{\cdot}COO^-$ radical ions, which consequently reduce Cd(II) and Cd(I) ions (Eqs. (10)–(12)):

$$\mathrm{HCOO^- + OH(H) \rightarrow {}^{\circ}COO^- + H_2O(H_2)} \tag{10}$$

$$\mathrm{Cd(II) + {}^{\circ}COO^- \rightarrow Cd(I) + CO_2} \tag{11}$$

$$\mathrm{Cd(I) + {}^{\circ}COO^- \rightarrow Cd(0) + CO_2} \tag{12}$$

Therefore, it causes the reduction of Cd (II) to Cd(0). In principle, the same mechanism is valid for solution containing Pb(II) ions.

If Cd(II) and Pb(II) ions are present in the sample simultaneously, Cd(II) reduction is observed after reduction of a considerable amounts of Pb(II) ions due to its lower reduction potential ($E^0_{\mathrm{Cd^{2+}/Cd}} = -0.403$ V and $E^0_{\mathrm{Pb^{2+}/Pb}} = -0.126$ V).

In the case of Cr(VI) ions, the EB treatment leads to the reduction of Cr(VI) to Cr(III).

3.2. *Effect of TiO_2 on the elimination of metal ions by optimum EB irradiation*

The effect of TiO_2 (as adsorbent and catalyst) on the removal efficiencies by EB irradiation was studied by adding different amounts of TiO_2 at a fixed radiation dose of 6 kGy (Fig. 2). As indicated the removal percentages of Cd(II), Pb(II) and Cr(VI) were 71.0% (±1.6%), 84.1% (±2.5%) and 82.8% (±3.6%), respectively, in the absence of TiO_2 (*X*-axis value = 0). However, when 0.1 g L^{-1} TiO_2 was added to the metal solutions, a significant removal enhancement to 86.0% (±2.5%), 94.3% (±1.8%) and 93.0% (±2.2%), respectively, was observed, which may be due to its sorption or/and EB–catalytic properties. As the amount of TiO_2 increased from 0.1 to 0.9 g L^{-1}, the removal efficiencies increased gradually to 96.0% (±3.8%), 99.1% (±2.7%) and 94.0% (±1.8%), respectively; eventually, these values decreased slightly at the concentration of 1 g L^{-1}. The negative impact of the increasing amount of TiO_2 beyond 0.9 g L^{-1} may be attributed to the overlapping active sites of TiO_2 at higher concentrations [22]. To investigate the occurrence probability of synergetic effect resulted from the combination of TiO_2 and EB radiation, the trends of the metal ions concentrations were considered in the presence of TiO_2 alone, i.e., without applying the EB radiation (Fig. 3).

The results displayed that the removal began immediately upon the addition of TiO_2, indicating its sorption properties toward the metal ions. According to this figure, as the amount of TiO_2 was increased up to 0.8 g L^{-1}, the removal efficiencies of Cd(II), Pb(II) and Cr(VI) were increased to 81.2% (±3.1%), 85.1% (±1.2%) and 78.0% (±2.5%), respectively. After that, the curve reached a plateau due to either overlapping active sites of TiO_2 or its equilibration achievement with the metal ions. High removal efficiencies in the presence of TiO_2 under the ambient (laboratory) conditions were partly because of their large surface areas and high activities caused by the size quantization effect in consistent with previous reports [23–25].

To carry out a thorough assessment of the TiO_2 effect on metal ions elimination with the radiation dose of 6 kGy, the removal efficiency for each metal ion under three processes (i.e., application of EB, TiO_2 and EB + TiO_2) was determined, and the results are illustrated in Fig. 4. Concerning this figure, one may realize that in all the three processes, the concentrations of metal ions in the solution decrease. As observed, the removal percentages of Cd(II), Pb(II) and Cr(VI), respectively, were 71.9% (±2.5%), 84.6% (± 1.6%) and 84.5% (±3.1%) by EB, and 81.2% (±1.8%), 85.1% (±2.4%) and 78.0% (±2.7%) by TiO_2 processes. Comparison of these results indicates that when EB radiation and TiO_2 were applied separately, the order of reduction for Cd(II), Pb(II) and Cr(VI) concentrations was Cd < Pb = Cr in presence of EB, which is in agreement with the reduction potential values, i.e., $E^0_{\mathrm{Cd^{2+}/Cd}} = -0.403\ \mathrm{V} < E^0_{\mathrm{Pb^{2+}/Pb}} = -0.126$ V. It is to be noted that despite the highest reduction potential ($E^0 = +1.33$ V) for Cr(VI)/Cr(III), its removal efficiency is similar to that of Pb(II), which is attributed to the pH dependency of Cr(VI) reduction, while this order is Cr < Cd < Pb in the presence of TiO_2 (the reasons are discussed under section 3.4). Moreover, the removal

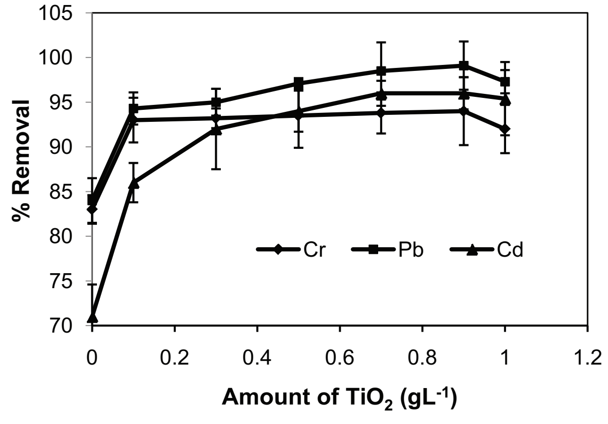

Fig. 2. Effect of TiO_2 dosage (g L^{-1}) on the removal efficiencies of Cd(II), Pb(II) and Cr(VI) ions irradiated by 6 kGy EB (conditions: sample volume – 20 mL; concentration of each metal ion – 10 mg L^{-1}; pH – 7.0; formate ion concentration – 1.3×10^{-3} mol L^{-1}).

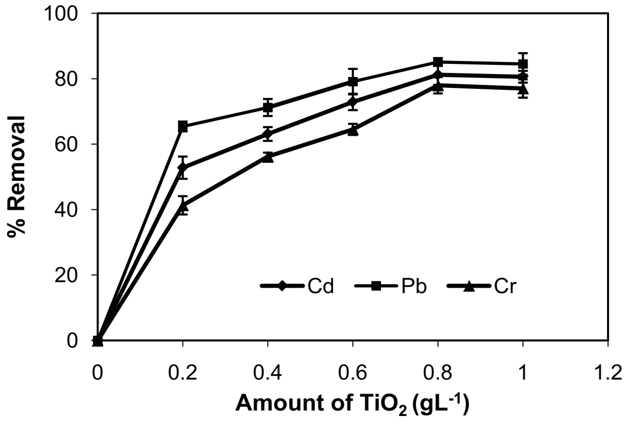

Fig. 3. The percentage removal of Cd(II), Pb(II) and Cr(VI) in the presence of TiO_2 without applying the EB radiation (conditions: sample volume – 20 mL; concentration of each metal ion – 10 mg L^{-1}; pH – 7.0; formate ion concentration – 1.3×10^{-3} mol L^{-1}).

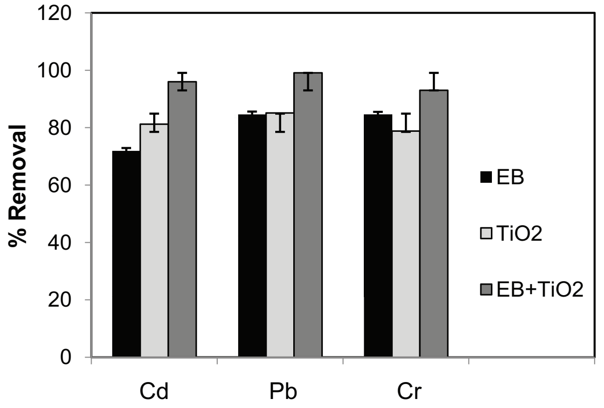

Fig. 4. The removal efficiencies of Cd(II), Pb(II) and Cr(VI) ions by different processes (conditions: radiation dose – 6 kGy; sample volume – 20 mL; concentration of each metal ion – 10 mg L^{-1}; pH – 7.0; formate ion concentration – 1.3 × 10^{-3} mol L^{-1}; amount of TiO_2 – 0.9 g L^{-1}).

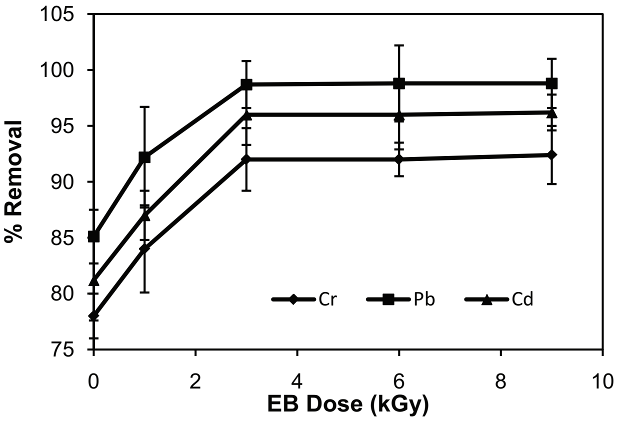

Fig. 5. The percentage removal of Cd(II), Pb(II) and Cr(VI) ions at different irradiation doses of EB (conditions: sample volume – 20 mL; concentration of each metal ion – 10 mg L^{-1}; pH – 7.0; formate ion concentration – 1.3 × 10^{-3} mol L^{-1}; amount of TiO_2 – 0.9 g L^{-1}).

efficiencies were more or less in the same range for both the cases (i.e., EB and TiO_2 processes). As an explanation, it is noteworthy that TiO_2 plays a dual role here, acting as adsorbent and photocatalyst as well. Due to the negative reduction potential values for Cd^{2+}/Cd and Pb^{2+}/Pb, the electrons generated by the two sources (EB and/or TiO_2) are balanced with the impact of Cd(II) and Pb(II) ions adsorptions onto TiO_2 surface. In the case of chromium, the positive reduction potential ($E^0Cr_2O_7^{2-}/Cr^{3+} = 1.33$) depicts the easiness of the ions reduction by EB, but due to the presence of CrO_4^{2-} anions at pH 7; the electrostatic attraction with the sorbent surface (as Ti–OH) decreases, leading to a partial equilibration for EB irradiation and photocatalytic processes.

On the other hand, when EB radiation and TiO_2 were applied simultaneously, the reduction of metal ions occurred more effectively (96.0% (±3.8%), 99.1% (±2.7%) and 93.0% (±1.8%)) for Cd, Pb and Cr, respectively). This outcome may pertain to the EB–catalytic reduction occurred through capturing the electrons released from TiO_2 (activated by EB radiation [12]) as well as radiolytic reactions by EB, causing interfacial and solution bulk reductions, respectively. Moreover, ionizing radiation may cause some charge dislocations on the adsorbent surface, and consequently, the adsorption of the metal ions from the solution occurs [26].

3.3. Coincident effect of TiO_2 and EB on the elimination of metal ions

In order to investigate the synergistic effect of the EB and TiO_2, the metal ion solutions containing 0.9 g L^{-1} TiO_2 nanopowder were irradiated with 1, 3, 6 and 9 kGy doses, and the removal percentages were obtained as the function of radiation dose (Fig. 5). As observed, the percentage removal of Cd(II), Pb(II) and Cr(VI) ions in presence of TiO_2 without applying EB were 81.2% (±3.6%), 85.1% (±2.4%) and 78.0% (±2.0%) due to adsorption onto TiO_2 and perhaps a weak photocatalytic effect under visible light. Whereas, by the application of 3 kGy EB, the removal efficiencies of 96.0% (±2.7%), 98.7% (±2.1%) and 91.8% (±2.8%) were achieved, respectively.

This observation can be attributed to either radiolytic reduction by EB or both the radiolytic and EB–catalytic reductions. However, an increase in the radiation dose up to 9 kGy didn't enhance the removal efficiencies considerably. Consequently, one may recognize that the appropriate dose for maximum removal of metal ions in the presence of TiO_2 is 3 kGy, which is lower than that of 6 kGy applied in the absence of TiO_2. This decrease of the applied radiation dose is due to the synergistic effect of TiO_2.

The activation of TiO_2 and the subsequent metal ions removal (Cr(VI) as example) in presence of EB and TiO_2 can be suggested as follows:

$$\mathrm{TiO_2} + \mathrm{EB} \rightarrow \mathrm{TiO_2} + e^-_{\mathrm{CB}} + h^+_{\mathrm{VB}} \tag{13}$$

$$\mathrm{Cr_2O_{7^{2-}}} + 14\mathrm{H}^+ + 6\mathrm{e}^- \rightarrow 2\mathrm{Cr}^{3+} + 7\mathrm{H_2O} \tag{14}$$

$$2\mathrm{H_2O} + 4\mathrm{h}^+ \rightarrow \mathrm{O_2} + 4\mathrm{H}^+ \tag{15}$$

Irradiation of TiO_2 by EB may produce the hole–electron pairs (Eq. (13)) at the surface of the photocatalyst. After the hole–electron pairs being separated, the electrons can reduce Cr(VI) to Cr(III) (Eq. (14)), and the holes may lead to generation of O_2 in the absence of any organics (Eq. (15)).

3.4. Effect of pH on the elimination of metal ions

The pH of solution is one of the most important parameters controlling the metal ion sorption and removal processes. It influences: (i) the surface charge of metal oxides (TiO_2) on one hand, i.e., below a particular pH value metal oxides possess a positive surface charge, whereas above that pH they have a negative surface charge; and (ii) the behavior and stability of metal ions on the other hand. The pH at the point where the surface charge is zero (pH_{pzc}) is 6 for TiO_2

[27]. According to another report, the concentration of the surface OH on TiO_2 strongly depends on solution pH [28]. When the solution pH is low (2–4), they are mainly present in the forms of Ti–OH and/or Ti–OH_2^+, at pH range of 4–8, it exists entirely as Ti–OH; when the solution pH is high, on the other hand, the surface OH of TiO_2 will be dissociated to form TiO^-. Hence, the pH effect on the removal efficiencies was investigated; the pH values of sample solutions containing metal ions were adjusted in the range of 2.0–10 and irradiated with 3 kGy dose after 2 h equilibration. As it is obvious from Fig. 6, the highest removal efficiencies (96.0% (±2.5%) and 98.7% (±2.3%), respectively) were found for Cd(II) and Pb(II) at pH range of 7.0–10, indicating that the electrostatic attraction between the positively charged metal ions (Cd^{2+} and Pb^{2+}) and the negative surface charge of TiO_2 dominates the adsorption (and consequent reduction). While these efficiencies decreased drastically in acidic pH due to electrostatic repulsion between the positive charges of metal ions and TiO_2 surface. In the case of Cr(VI) the quantitative removal (>96%) was obtained in the pH range of 2–4. It is well known that Cr(VI) exists mainly in the form of $HCrO_4^-$ and $Cr_2O_7^{2-}$ (in equilibrium) at pH < 6, and as CrO_4^{2-} at pH > 6 [29,30]. Moreover, the reduction potential of Cr(VI) to Cr(III) is pH dependent, and the thermodynamic driving force of Cr(VI) reduction decreases with increasing pH (Eqs. (16)–(18)). Hence, it is readily reduced in acidic pH (Eqs. (16) and (17)). In neutral and alkaline pH, CrO_4^{2-} is dominant species, which is not reduced (Eq. (18)) as readily as other two species.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad E^0 = 1.33V \tag{16}$$

$$HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O \quad E^0 = 1.35V \tag{17}$$

$$CrO_4^{2-} + 4H_2O + 3e^- \rightarrow Cr(OH)_3 + 5OH^- \quad E^0 = 0.13V \tag{18}$$

At low pH, negatively charged $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions can adsorb onto TiO_2 surfaces via electrostatic attraction with positively charged Ti–OH_2^+. On the contrary, in the high pH region, there is an electrostatic repulsion between negatively charged CrO_4^{2-} and TiO^-, resulting in the loss of Cr(VI) removal efficiency. So that, under the acidic pH, the presence of negatively charged Cr(VI) ions causes the more removal of Cr(VI) by TiO_2 than neutral pH [31].

However, in order to avoid hydrolysis of the metal ions (at higher pH values) and application of buffer solution, and also to achieve the simultaneous elimination of the three metal ions, pH value of 7.0 was selected for subsequent experiments.

Furthermore, in order to study the possibility of metal ions precipitation due to their hydroxide formation, the effect of pH on the variation of metal ions concentrations was investigated in the absence of both EB and TiO_2, and observed that only Cr(VI) concentration was negligibly reduced by just 0.76% at pH 7.0. The same statement could be made from the intercepts of Figs. 1 and 3 (being 0 in both cases).

3.5. Effect of contact time on removal efficiency, kinetic modeling

In order to study the time effect on the removal efficiencies of desired metal ions by EB/TiO_2, since the EB irradiation is a fast process (velocity of 16.6 cm s^{-1}); only the kinetics of adsorption/photocatalytic processes by TiO_2 was investigated.

The nature of adsorption process depends on physical or chemical characteristics of the adsorbent and on the adsorption system conditions too. The kinetic studies were performed in the presence of 0.9 g L^{-1} TiO_2 and optimum solution pH for each metal ion with 10 mg L^{-1} concentrations at constant temperature (25°C ± 0.5°C) and stirring rate (300 rpm), under the purging of N_2 gas. Sampling was done at different mixing time intervals (0–120 min) and measured the concentrations immediately after irradiation with constant 3 kGy dose.

Fig. 7 shows the plot of the removal percentages vs. contact time. From this figure, it was observed that immediately

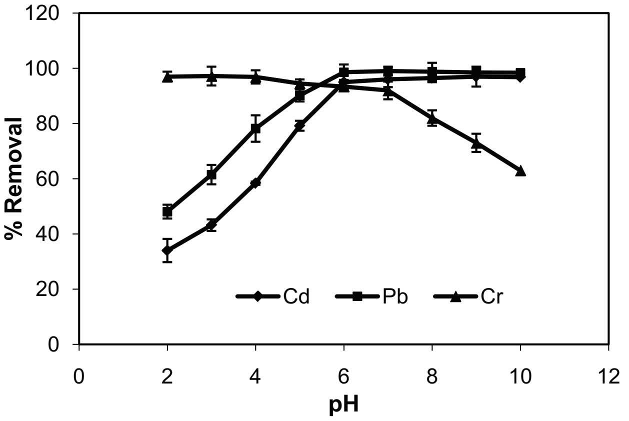

Fig. 6. Effect of pH on the removal efficiencies of Cd(II), Pb(II) and Cr(VI) ions (conditions: radiation dose – 3 kGy; sample volume – 20 mL; concentration of each metal ion – 10 mg L^{-1}; formate ion concentration – 1.3 × 10^{-3} mol L^{-1}; amount of TiO_2 – 0.9 g L^{-1}).

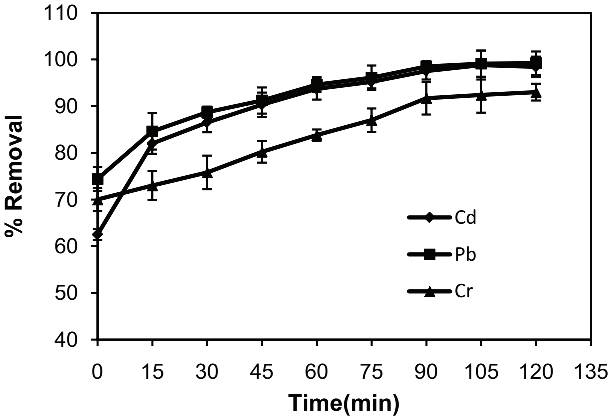

Fig. 7. Effect of contact time on the removal efficiency (conditions: sample volume – 20 mL; concentration of each metal ion – 10 mg L^{-1}; pH – 7.0; formate ion concentration – 1.3 × 10^{-3} mol L^{-1}; amount of TiO_2 – 0.9 g L^{-1}).

after TiO_2 addition (without stirring, i.e., zero time), and applying radiation dose of 3 kGy, the removal efficiencies of all three metal ions were above 60%. This observation is attributed to the EB radiation and photocatalytic behavior of TiO_2. However, by increasing the contact time up to 90 min, the efficiencies were increased to higher than 90% (may be due to increased number of vacant sites available on TiO_2 surface and/or increased hole–electron pairs); as a result, there exists an increased concentration gradient between the adsorbate in solution and at the adsorbent surface. This increase in concentration gradient tended to increase in metal ions adsorption rate and then after remained almost constant. Hence, although same results were observed for 90 and 120 min, 120 min (2 h) was chosen as optimum contact time to ensure the equilibration. Moreover, it can be concluded from the slopes of the curves that the removal of Cr(VI) is mainly through the radiolytic reduction in the bulk solution, while that of Cd(II) and Pb(II) is by sorption and reduction at the TiO_2 surface. The highest slope (with lowest initial removal efficiency of 62%) for Cd(II) is due to its lowest reduction potential. The kinetics of adsorption was analyzed using kinetic models of zero-, first-, and second-order. From this evaluation, the reduction pattern was better fitted to and described by the first-order kinetic model. The adsorption kinetics can be described adequately by a simplified first-order rate equation (Eq. (19)):

$$\ln\left[{C_0}/{C_t}\right] = k_1 t \tag{19}$$

where C_0 and C_t are the metal ions concentrations at initial stage and at time t, respectively. k_1 is the rate constant, and t is the reaction time. The k values (Table 1) were obtained from the slope of the linear regression plot of $\ln[C_0/C_t]$ vs. time (figure not presented).

3.6. Real sample analysis and method validation

The method was applied to the wastewaters obtained from petroleum refineries and paint factories as the two sources of heavy metals. Samples were collected from an oil refinery and paint factory effluents from southern and central parts of Iran, respectively. The samples were filtered and irradiated by EB under the optimal conditions (TiO_2 = 0.9 g L^{-1}, pH = 7.0, stirring time = 2 h, EB dose =3 kGy in the presence of 1.3×10^{-3} mol L^{-1} sodium formate). Then, the concentrations of Cd(II), Pb(II) and Cr(VI) ions in wastewater samples were determined prior to and following the treatment process. Table 2 presents the percentage removal of the metal ions in both samples. According to the results gained by this method in the petroleum samples 94.6% (±1.7%), 95.7% (±1.8%) and 91.2% (±2.7%) and in the paint wastewater 95.2% (±2.8%), 96.5% (±2.3%) and 90.4% (±3.6%), removal efficiencies were obtained for Cd(II), Pb(II) and Cr(VI) ions, respectively. Obviously, these lower yields of metal ions removal in comparison with the obtained experimental results for the synthetic wastewater are attributed to the matrix complexity of the real samples. The findings indicated that when EB and TiO_2 were applied together in order to remove the metal ions from these samples, more than 90.0% removal was obtained suggesting the application of this method as a promising technique for the industrial wastewater treatment. The method validation was performed by recovery experiments for spiked samples (Table 3). The obtained results are in good agreement with added amounts, indicating the reliability and capability of the method for real samples.

Table 1
Kinetic parameters for the removal of Cd(II), Pb(II) and Cr(VI) by EB/TiO_2 in the optimum conditions

Kinetic models and parameters						
Metal ion	Zero-order		First-order		Second-order	
	k_0 (mol L^{-1} min^{-1})	R^2	k_1 (min^{-1})	R^2	k_2 (L mol^{-1} min^{-1})	R^2
Cd	0.2454	0.7568	0.0276	0.9681	0.0061	0.7741
Pb	0.1858	0.8567	0.0303	0.9761	0.8046	0.8046
Cr	0.233	0.965	0.0144	0.9672	0.0011	0.8974

Table 2
Removal efficiency of the heavy metals from real wastewater samples

Metal ion	Initial concentration (mg L^{-1})		Removal efficiency (%)[c]	
	Pet. refinery[a]	Paint fact.[b]	Pet. refinery	Paint fact.
Cd(II)	0.9	0.7	94.6 (±1.7)	95.2 (±2.8)
Pb(II)	1.8	1.4	95.7 (±1.8)	96.5 (±2.3)
Cr(VI)	0.7	1.2	91.2 (±2.7)	90.4 (±3.6)

[a] Petroleum refinery wastewater. Samples obtained from southern part of Iran.

[b] Paint factory wastewater. Samples obtained from central part of Iran.

[c] Average of triplicate analyses (±standard deviation).

4. Conclusions

The results of the removal efficiencies obtained for the synthetic and real wastewater samples confirmed that the combination of EB irradiation with TiO_2 addition is an effective way of lowering the Cd(II), Pb(II) and Cr(VI) contents of wastewater. The removal percentages of the metal ions depend on the solution pH, amount of TiO_2 and the radiation dose. Each process (i.e., surface adsorption and radiolytic reaction by EB irradiation) is capable of removing the metals of interest individually up to certain extent.

However, the combination of the two processes seems to activate TiO_2 and causes the EB–catalytic reduction of metal ions as well. The radiation dose required for the removal of metal ions in the presence of TiO_2 was effectively decreased due to its synergistic effect. Hence it can be concluded that the net metal removal mechanism is the result of three steps (processes), namely adsorption, radiolytic reduction and EB–catalytic reduction. Since no secondary pollutant materials are produced by ionizing radiation, this method is an environmentally benign process for the toxic metals removal in large scale.

The comparative data with some previous reports for the removal of metal ions by UV/TiO_2 method are given in Table 4. As it is evident, our results are comparable with and, in some cases, better than other reports by considering the removal efficiencies on one hand. On the other hand,

Table 3
Determination of Cd(II), Pb(II) and Cr(VI) and method validation (n = 3)

Sample of wastewater[a]	Contaminant	Added (mg L^{-1})	Found (mg L^{-1})[b]	Recovery (%)
Petroleum refinery	Cd	0.0	0.9 (±3.5)	–
		10.0	10.7 (±2.8)	98.0
	Pb	0.0	1.8 (±2.6)	–
		10.0	11.7 (±3.9)	99.0
	Cr	0.0	0.7 (±4.3)	–
		10.0	10.5 (±3.2)	98.0
Paint factory	Cd	0.0	0.7 (±2.2)	–
		10.0	10.5 (±3.1)	98.0
	Pb	0.0	1.4 (±2.5)	–
		10.0	11.5 (±2.1)	101.0
	Cr	0.0	1.2 (±3.6)	–
		10.0	10.9 (±3.5)	97.0

[a] Collected from an oil refinery and a paint factory effluents from southern and central parts of Iran, respectively.
[b] Average values (±standard deviation) for three replicate measurements.

Table 4
Comparison of the proposed method with UV/TiO_2 reports

Metal ion	Intial concentration (mg L^{-1})	TiO_2 dose (g L^{-1})	Irradiation condition	Removal efficiency (%)	References
Cr(VI)	10	1	120 min UV	100	[32]
Cd(II)	10	50	24 h UV	15.2	[33]
Cr(VI)	10	50	24 h UV	77.7	
Pb(II)	10	50	24 h UV	58.8	
Cd(II)	25	0.9	120 min UV	99.8	[34]
Pb(II)	25	0.9	120 min UV	99.2	
Pb (II)	50	0.6	180 min UV	96.8	[35]
Cr(VI)	50	5	180 min UV	96.8	[36]
Cr(VI)	42	2	60 min UV	94.0	[37]
Cd(II)	30	1.5	30 min UV	100	[38]
Cr(VI)	60	0.5	30 min UV	91.6	[39]
Cd(II)	10	0.9	3 kGy EB few seconds	98.8	This work
Cr(VI)	10	0.9	3 kGy EB few seconds	92.4	
Pb(II)	10	0.9	3 kGy EB few seconds	99.1	

the irradiation time proved better in present work than the other reported values; that means our technique is much faster than reported works.

Acknowledgments

The authors express their appreciation to the Graduate Studies and Research Council of the University of Zanjan for financial support for this work. The authors are also grateful to Yazd Radiation Processing Center (YRPC) for irradiation services supplied.

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