



Removal of heavy metals (Cu²⁺ and Cd²⁺) from effluent using gamma irradiation, titanium dioxide nanoparticles and methanol

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Abstract

Heavy metal pollution has become one of the most serious environmental problems. The aim of this study was to achieve an efficient treatment process of effluents containing 1 mM copper (Cu²⁺) and cadmium (Cd²⁺) ions using a combination of gamma irradiation, methanol and TiO₂ nanoparticles under different pH values. The results showed that in acidic conditions, removal of Cu²⁺ and Cd²⁺ ions by physical adsorption was less than 15% and adsorption of Cd²⁺ was more than that of Cu²⁺. In the same condition, the Cu²⁺ removal percentage by irradiation was greater than that of Cd²⁺. In basic solutions, due to precipitation of Cd and Cu hydroxides, it was not possible to carry out adsorption experiments on Cd²⁺ and Cu²⁺ ions removal by TiO₂ and gamma irradiation. Cu²⁺ and Cd²⁺ ions removal processes under different conditions could be depicted by the first order kinetics model. The combined application of TiO₂ and methanol enhanced Cu²⁺ and Cd²⁺ ions removal at all pH levels examined. However, using the combination of TiO₂ and methanol at acidic solutions facilitated completely removal of Cu²⁺ and Cd²⁺ ions. So that, only using 50 kGy irradiation dose with combination of TiO₂ nanoparticles and methanol led to the removal of 99% of coexisting Cu²⁺ and Cd²⁺ ions from the acidic wastewater.

Keywords Gamma irradiation · Heavy metals · Methanol · Nanoparticles · Radiocatalysis · Wastewater

Introduction

Heavy metal pollution is one of the major ecological concern on world scale due to its dramatically increase caused by both anthropogenic and natural sources [1]. However, a dramatic increase of heavy metals into the environment related to anthropogenic activity such as untreated urban sewage sludge discharge, mining, industrial wastes, smelting and so many other human activities [2]. The occurrence of high levels of toxic metals in the environment has a potential threat to the human [3]. In this context, environmental exposure to cadmium (Cd²⁺) and copper (Cu²⁺) ions are

associated with health effects on various organs, including bone demineralization, lung cancer, renal disease, and liver injury. [4].

Nowadays, it is well known that aquatic ecosystems are directly or indirectly the end destinations of these substances [3] and to preserve environmental quality, management of wastewater containing heavy metals has been one of the most prominent challenges in the past few decades [5]. However, the commonly used procedures to remove the toxic heavy metals (Cu²⁺ and Cd²⁺) from wastewater before discharge into the environment include ion exchange, chemical precipitation, adsorption, membrane filtration, supercritical fluid extraction, electrochemical process, advanced oxidation process and membrane bio-reactors [6]. Most of these methods still present limitations in terms of their high installation costs, secondary pollution and complex operation [7]. To overcome such limitations, the development of new eco-friendly methods to reach high removal efficiencies is always highly desired [8–10]. Impressively, different types of adsorbents were prepared such as layered double hydroxide-based nano-materials [7], metal–organic framework-based materials [8], boron nitride-based materials [9] and polymer-based

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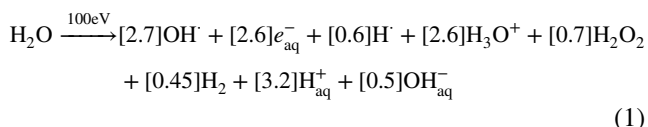
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nanocomposites [10] has recently received increasing attention for its merits as a highly efficient, versatile and easy-to-operate technique for removal of inorganic pollutants (e.g., heavy metal ions) from wastewater solution.

Radiation treatment including ionizing radiation (gamma ray, high-energy electrons, etc.) is an emerging wastewater treatment technology for purification of water, municipal and industrial wastewater [11] and can be utilized for the reduction of certain metal ions to insoluble forms [12]. Gamma irradiation process generates several chemical species simultaneously at nearly equal amount oxidizing and reducing species in water radiolysis as described in Eq. 1 including hydroxyl radical (OH[•]), solvated or hydrated electrons (e_{aq}^-), and hydrogen atoms (H[•]) [13, 14]. The radiation yield of these chemical species in term of G-values is given in brackets, which was defined as the number of produced or decomposed molecule per 100 eV absorbed energy at pH 7 ($\times 10^{-7}$ mol j⁻¹) [15]. Among the product formed, OH[•] radical is a strong oxidant with an oxidation potential of 2.72 V, whereas e_{aq}^- and H[•] is a powerful species with a reduction potential of -2.9 and -2.3 V, respectively [14]. These radiolysis products are primarily responsible for the degradation of water pollutants by ionizing radiation [13].



A single using of ionizing radiation requires sufficiently high absorbed doses to reach a higher removal of the substance, which is not economically acceptable for practical application [11]. In these regards, ionizing radiation is better combined with other techniques such as radiocatalysis and chemical additives to improve the degradation efficacy and reduce the cost [14, 16].

Previous studies focused mostly on the treatment of some heavy metals from water using single ionizing radiation [5, 12, 17] or photocatalysis [18, 19]. However, the literature review showed there is a lack of published studies on the removal of Cu²⁺ and Cd²⁺ ions from water and wastewater by gamma irradiation and its combination with TiO₂ radiocatalyst and methanol. Radiocatalysis is a process that merges photocatalysis and radiolysis [20]. However, unlike photocatalysis, the mechanism of radiocatalysis reaction has not been fully investigated [21] and expected to be similar to photocatalysis, where the gamma radiation excites the oxides to produce electrons and holes in the surface [20]. Hence, this study aims to evaluate the integrated effects of different factors such as solution pH, nano-sized TiO₂ catalyst (radiocatalyst) and methanol (OH[•] radical scavenger) on removal efficiency of Cu²⁺ and Cd²⁺ ions from wastewater by different levels of gamma irradiation.

Experimental procedures

Materials and methods

Analytical grade salts of heavy metals [Cd(NO₃)₂·4H₂O and Cu(NO₃)₂·3H₂O, ≥99%] were supplied from Merck Company and dissolved into effluent from a Municipal Wastewater Treatment Plant (MWTP) to prepare solutions with a final concentration of 1 mM Cd²⁺ and Cu²⁺ ions. The nitrate anion metal salts instead of chloride were selected due to better dissociation and hence increased the extent of metals photocatalytic reduction reported by Khalil et al. [19]. Approximately 20 L of effluent was collected in a sterilized special recipient before the chlorination treatment. The effluent was used after filtration by 0.45 μm Whatman filter paper. Chemical properties of effluent used in this study were summarized in Table 1. The effects of solution pH and additives such as TiO₂ nanoparticles (NPs) and methanol (MeOH) on removal of Cd²⁺ and Cu²⁺ ions were investigated. Solution pH levels were acidic (4.5) and basic (9.0 and 12) and were adjusted using 0.1 M HCl and 0.1 M NaOH solutions. The pH levels used in this research selected with taking into account pK_a equations of oxidizing species (Eqs. 2, 3, 4) [22, 23] occurrence forms of heavy metals [17] and surface charge of NPs (Eqs. 5, 6) [18]. MeOH (CH₃OH, ≥99.9%) and TiO₂ NPs powder (Degussa P25 consisting of 80% anatase and 20% rutile) were purchased from Merck and Degussa Companies (Evonik Industries, Germany), respectively. Specific surface area and average particle size of TiO₂ NPs powder are about 50 m² g⁻¹ and 21 nm, respectively, and confirmed by transmission electron microscopy (TEM) and scanning electron microscope (SEM) imaging as introduced by the manufacturer company (Fig. 1). For TiO₂ NPs treatment, it was dispersed in the solution at a concentration of 2 g L⁻¹ and was magnetically

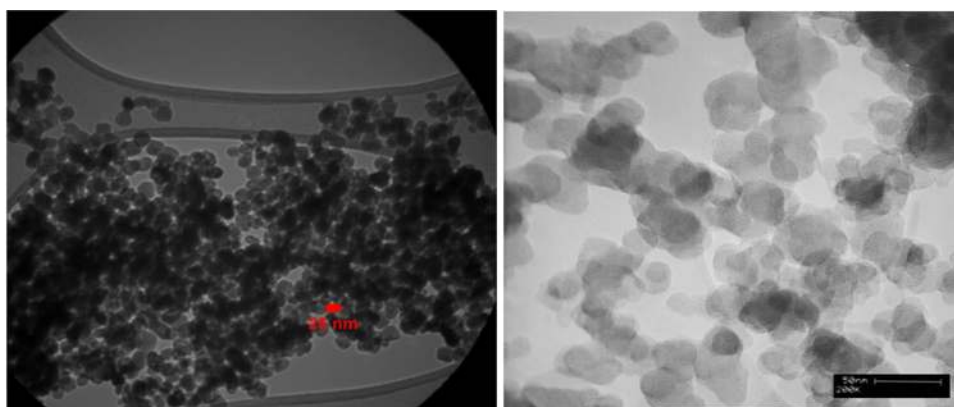
Table 1 Chemical properties of effluent used in this study

Characteristics	Content	Characteristics	Content (mg L ⁻¹)
pH	7.54	Ca	43.1
EC (dS m ⁻¹)	1.07	Mg	15.3
NO ₃ ⁻ (mg L ⁻¹)	49.1	Cd	ND
Turbidity (NTU)*	6.05	Pb	1.03
BOD ₅ (mg L ⁻¹)	27.5	Cu	0.353
COD (mg L ⁻¹)	91.7	Zn	0.738
P (mg L ⁻¹)	2.84	Mn	0.152
K (mg L ⁻¹)	20.4	Ni	0.229
Na (mg L ⁻¹)	112.5	Fe	0.319

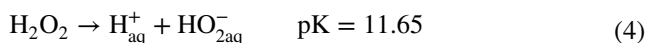
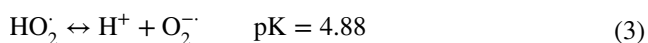
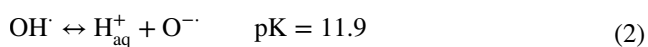
ND non-detected

*Nephelometric turbidity units

Fig. 1 Transmission electron microscopy (TEM, left) and scanning electron microscope (SEM, right) images of TiO₂ P25 nanoparticles



stirred to ensure homogeneous distribution of the radiocatalysts throughout the solution during irradiation [19]. MeOH as OH[•] radical and valence band holes scavenger was added at a concentration of 10% by volume to decrease oxidizing species and reduce electron–hole recombination. MeOH concentration was selected based on 1% it is destroying at the absorbed dose of 1 kGy [13] and high doses used in this research. Solution pH was recorded in the presence and absence of 2 g L⁻¹ TiO₂ NPs [16] and 10% (v/v) MeOH and the pH of mentioned treatments was adjusted to 4.5, 9 and 12 after MeOH and TiO₂ NPs additions. The physical adsorption of metal ions by the TiO₂ NP powder in the suspension systems was confirmed by measurements without irradiation (removal after allowing to stand 48 h to reach equilibrium by dark reaction) [18]. To eliminate over- and underestimation of physical adsorption, the dark reaction was carried out under average time of sample irradiation and held under similar environmental conditions for samples being irradiated. After centrifuging of samples with and without gamma irradiation (control or physical adsorption) for 10 min at a relative centrifugal force (RCF) 2810×g, the Cd²⁺ and Cu²⁺ concentrations were determined.



$$E_{\text{cb}}(V) = -0.05 - 0.059 \text{pH (at } 25 \text{ }^{\circ}\text{C)} \quad (5)$$

$$E_{\text{vb}}(V) = 3.15 - 0.059 \text{pH (at } 25 \text{ }^{\circ}\text{C)} \quad (6)$$

Gamma irradiation

Samples (50 mL each) were exposed to gamma rays at room temperature from a gamma cell ⁶⁰Co source (with dose rate of 432 Gy h⁻¹ and specific activity of 1000 Ci) with different absorbed doses of 0, 5, 10 and 20 kGy at the Nuclear

Agriculture Research School, Nuclear Science and Technology Research Institute, Karaj, Iran. In this study lower dose was not chosen because irradiation with lower dose was not sufficient for complete removal of heavy metals from solution [5]. The dose of radiation was determined by the standard Fricke dosimeter.

Sample analysis

Some chemical characteristics of effluent used in this study including biochemical oxygen demand (BOD₅) (method 5210B), chemical oxygen demand (COD) (method 5220B), pH and EC (methods 4500-H⁺ B and 2510 B, respectively), turbidity (method 2130 B), nitrate (NO₃⁻-N) (method 4500-NO₃ B), phosphate (P) (method 4500-P E), potassium (K) and sodium (Na) by flame photometer (methods 3500-K B and 3500-Na B, respectively), calcium (Ca), magnesium (Mg), manganese (Mn), lead (Pb), zinc (Zn), iron (Fe), Cu and Cd by direct air-acetylene flame atomic absorption spectrophotometer (method 3111B) according to the “Standard Methods for the Examination of Water and Wastewater” [24] were determined. In addition, the concentrations of dissolved Cu²⁺ and Cd²⁺ ions in irradiated and non-irradiated samples after centrifuging (Selecta lab, model T1 320) were measured as mentioned above method (method 3111B). Overall, concentrations of Ca, Mg, Cu, Zn, Pb, Cd, Fe, Mn and Ni were analyzed using atomic absorption spectrophotometer Shimadzu model AA-6300, Japan, Na and K by flame photometer, Corning-410, pH by pH meter model Mettler Toledo Instrument Co. Ltd., MA235, electrical conductivity (EC) by JENWAY EC meter model 4320, P by SU6100 spectrophotometer, Philler Scientific, USA, Turbidity by turbidity meter AL250T-IR and NO₃⁻-N by spectrophotometer Optizen 2120 UV.

Metal ions removal efficiency and radiation chemical yield of solute (G-value)

The G-value is defined as the number of species (e.g., molecules, radicals, and ions) changed in solutions by absorbing

100 eV of energy. The G-value and removal efficiency (η) can be calculated for pollutant using the following equations:

$$G\text{-value} = \frac{[(C_0 - C) \times N_A]}{(D \times 6.24 \times 10^{19})}, \quad (7)$$

$$\eta(\%) = \frac{(C_0 - C)}{C_0} \times 100, \quad (8)$$

where C_0 (mol L⁻¹) is the initial concentration of solute (before irradiation), C (mol L⁻¹) concentration of solute after irradiation at the applied dose, N_A Avogadro's number (6.023×10^{23} molecules mol⁻¹), D absorbed dose (kGy), 6.24×10^{19} conversion constant from kGy to 100 eV L⁻¹ and η degradation efficiency (%) [15, 23].

Dose constant

Dose constant (K_1) was calculated from the slope of the natural logarithm (ln) of the metal ion concentrations in mol L⁻¹ versus the dose (kGy). Dose constant (K_1) was used to calculate the dose required for 90 and 99% of solute removal ($D_{0.9}$ and $D_{0.99}$, respectively) using the following equations [15, 23]:

$$D_{0.9} = \frac{\ln 10}{K_1}, \quad (9)$$

$$D_{0.99} = \frac{\ln 99}{K_1}. \quad (10)$$

Statistical analysis

Data were subjected to analysis of variance as two factorial experiments ($4 \times 2 \times 2$ in acidic and $4 \times 2 \times 2 \times 2$ in basic conditions) with three replications ($n = 3$) based on completely randomized design using SAS software (computer SAS software version 9.1; CoHort Software). Finally, 16 and 32 treatments in acidic and basic solutions, respectively, were applied based on combinations of absorbed doses (0, 5, 10 and 20 kGy), pH (4.5, 9.0 and 12), MeOH (0 and 10%, v/v) and TiO₂ NPs (0 and 2 g L⁻¹). Duncan's multiple range test ($p < 0.05$) was used to evaluate the significance of differences between the treatments means. All quantitative data were shown as the mean \pm standard error. The Excel software (Excel software 2013, Microsoft Inc., WA, USA) was used to draw figures.

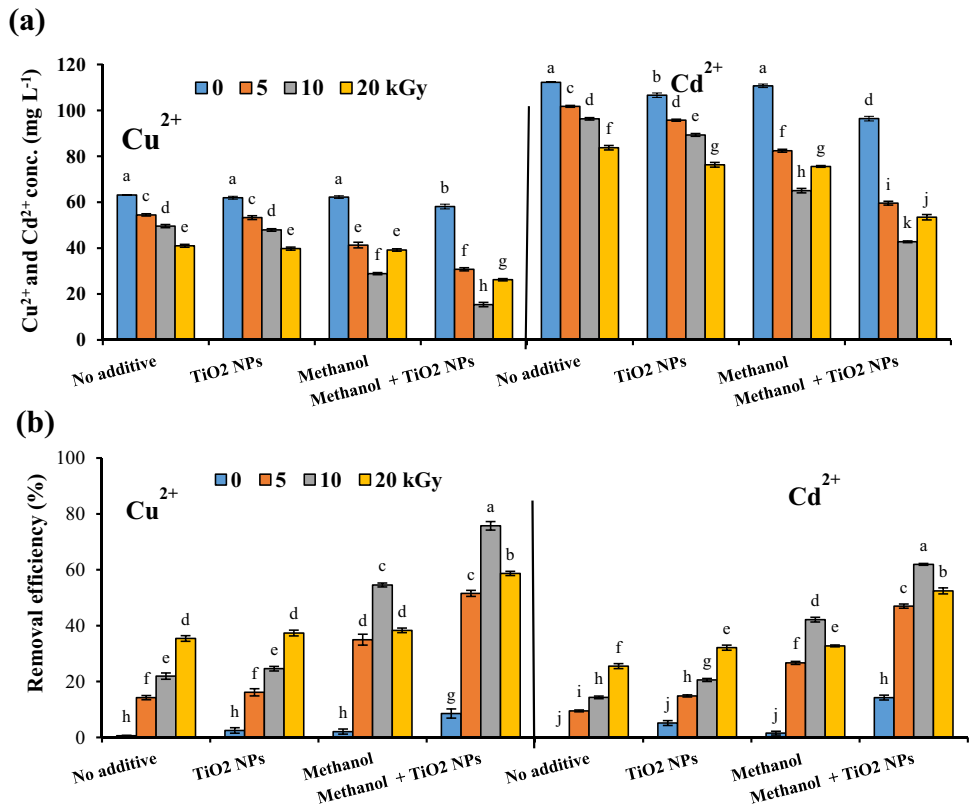
Results and discussion

Dark reaction or physical adsorption of Cu²⁺ and Cd²⁺ ions from aqueous solution in different conditions

The effects of pH, TiO₂ NPs and MeOH on the removal of heavy metals (Cu²⁺ and Cd²⁺) by dark adsorption were summarized in Figs. 2a, 3a and b. As seen, the removal of Cd²⁺ and Cu²⁺ ions was affected by pH and additives; so that the most of the Cd²⁺ and Cu²⁺ (≥ 90 and 95%, respectively) were removed under pH ≥ 9.0 with and without MeOH and TiO₂ NPs additions. It is well known that in the pH $> \text{pH}_{zpc}$ (pH 9.0 and 12) the surface charge of TiO₂ NPs is negative [25] and a significantly high electrostatic repulsive forces exists between the negatively charged sites of the adsorbent and Cu(OH)₃⁻, Cu(OH)₄²⁻, Cd(OH)₃⁻ and Cd(OH)₄²⁻ ions (predominant species at higher pH region), and thus results in a decrease in the adsorption capacity. With addition of MeOH, it can be adsorbed on TiO₂ NPs surfaces either molecularly or dissociatively [26] and affects the adsorption of the metal ions from solution. At alkaline solution, MeOH is deprotonated and negatively charged [27]; because of negative–negative electrostatic repulsion, MeOH adsorption is strongly retarded. According to these results, precipitation, and not adsorption, was responsible for the removal of Cu²⁺ and Cd²⁺ ions.

In addition, both Cu²⁺ and Cd²⁺ ions could be effectively removed by the combined application of MeOH and TiO₂ NPs under acidic pH condition, although using of TiO₂ NPs alone significantly increased adsorption of Cd²⁺. Generally, removal of Cu²⁺ and Cd²⁺ ions by physical adsorption in different treatments was less than 15% and adsorption of Cd²⁺ was better than Cu²⁺ (Fig. 2a). It is well-established that in the pH $< \text{pH}_{zpc}$ (pH 4.5), the positively charged sites of nano-adsorbent dominate or the number of negatively charged sites decreases [28], this enhances the repulsion forces existing between the NPs surface and the Cu²⁺ and Cd²⁺ ions (predominant species at lower pH region), and therefore decreases the ions adsorption. However, the excess adsorption of Cd²⁺ rather than Cu²⁺ could be attributed to competitive adsorption ability varies from one metal to another that is related to many factors, such as molecular mass, ion charge, hydrated ionic radius and hydration energy of the metals [28]. It is believed that partial dehydration of the hydrated Cd²⁺ and Cu²⁺ ions (predominant ions under acidic pH condition) must have occurred to adsorb on the surface of adsorbent and among the two metals assayed, Cd²⁺ with the lowest hydration energy (1807 kJ mol⁻¹) relative to Cu²⁺ (2100 kJ mol⁻¹) [29], may facilitate the hydrated Cd²⁺ ions more easily adsorbing on the NPs. After application of

Fig. 2 Effects of gamma, gamma + TiO₂ NPs, gamma + methanol and gamma + methanol + TiO₂ NPs treatments on concentrations (a) and removal efficiency (b) of Cd²⁺ and Cu²⁺ ions in acidic solution (pH 4.5). Values followed by the same letter are not significantly different at $p \leq 0.05$ by Duncan's multiple range test

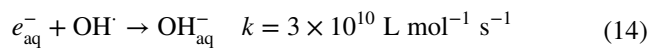
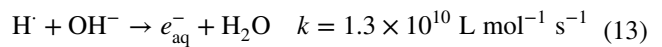
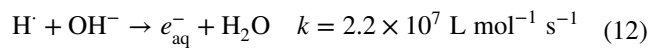
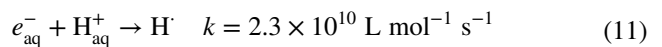


MeOH at low pH condition, this molecule can be adsorbed on the oxidized surface of TiO₂ NPs through the formation of a hydrogen bond with free surface hydroxyl groups or with a bridging oxygen anion [30]. So that, using MeOH and MeOH + TiO₂ NPs in dark reaction, Cu²⁺ and Cd²⁺ ions could be removed by interaction between divalent metal ions and substituents of MeOH such as hydroxyl (OH), etc., and then be adsorbed on TiO₂ NPs surface and be precipitated as a result of dark reaction. The mechanisms of interactions between carbonyl, hydroxyl, and carboxyl groups of humic acid to remove Cu²⁺, Co²⁺ and Sr²⁺ ions from wastewater have been reported by Zaki and El-Gendy [5]. Generally, in pH 4.5, no precipitation in dark reaction and little removal was observed due to the adsorption process (Fig. 2a).

Effect of solution pH on Cu²⁺ and Cd²⁺ ions removal by gamma irradiation

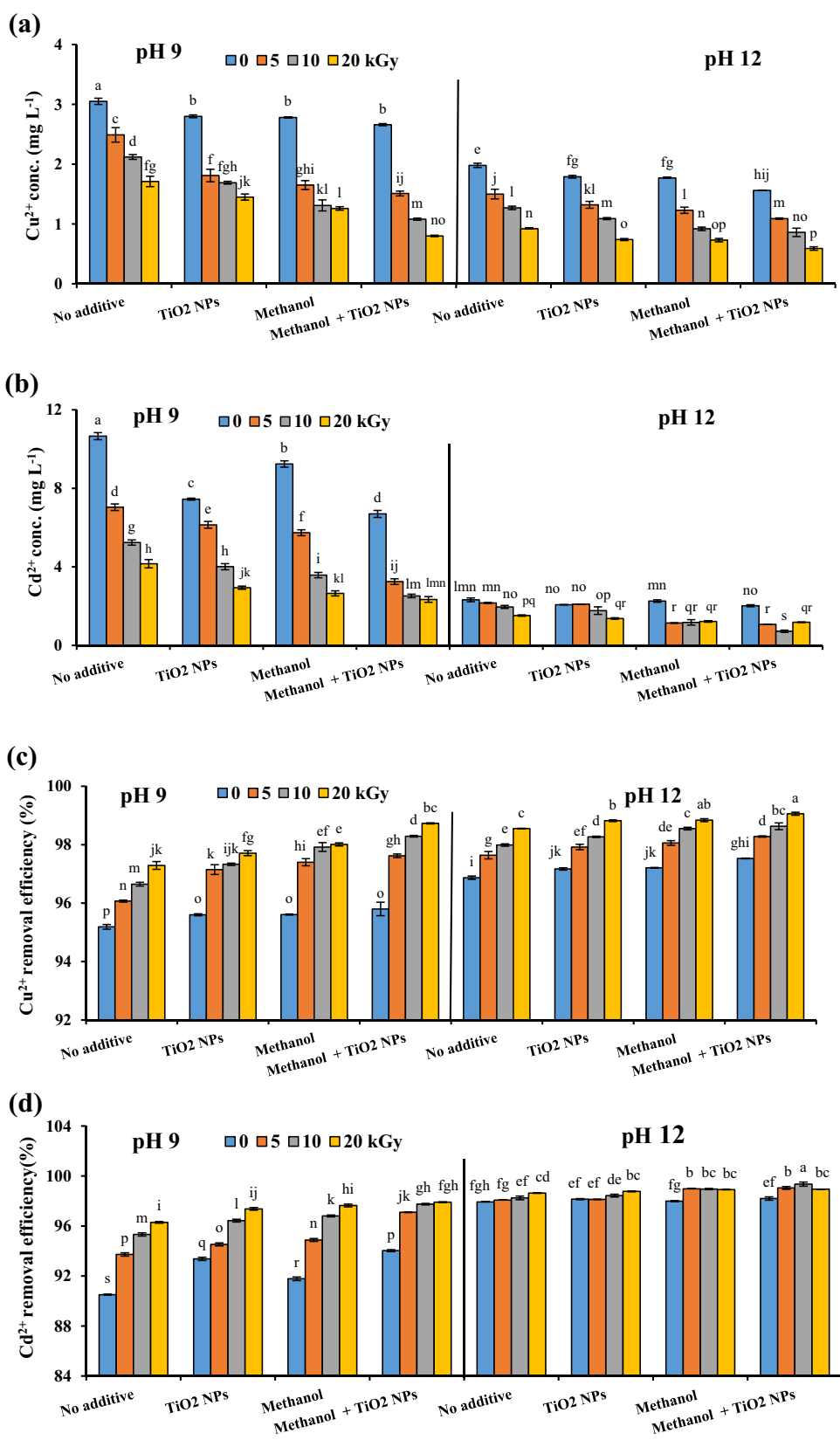
Increasing of pH values to 9.0 and 12 resulted in precipitation of Cd and Cu hydroxides and due to uncertainty to the results, it was not possible to carry out irradiation effects on removal of Cu²⁺ and Cd²⁺ ions at higher pH values (Fig. 3a, b). At low pH values (Fig. 2a, b), the removal of Cu²⁺ and Cd²⁺ ions through using different doses of gamma irradiation can be effective. However, high removal percentages were achieved at high absorbed doses. In other

words, by increasing irradiation dose, the radical species and removal efficiency were increased. For example, in pH 4.5 and absorbed dose 20 kGy, the removal percentages of Cu²⁺ and Cd²⁺ ions reached 35.4 and 25.5%, respectively (Fig. 2b). Generally, it was shown that the kinds of reactive species (Eqs. 2, 3, 4 and 11, 12, 13, 14) and occurrence forms of pollutants are dependent on the solution pH [17]. Therefore, the value of pH is an important factor to affect metal ions removal by ionizing radiation.



In addition, in aqueous solution, speciation of Cu²⁺ and Cd²⁺ ions showed that the solution pH determines their occurrence forms to a great extent. Cu²⁺ and Cd²⁺ ions predominate in the pH range of 3–6 and 3–8, respectively. At pH values above 8.0 and 11, all Cu and Cd exist as hydroxo-complexes. For example, Cu(OH)⁺, Cu(OH)₂^o,

Fig. 3 Effects of gamma, gamma + TiO₂ NPs, gamma + methanol and gamma + methanol + TiO₂ NPs treatments on Cu²⁺ and Cd²⁺ concentrations (a, b) and removal efficiency (c and d) in basic solutions (pH 9 and 12). Values followed by the same letter are not significantly different at $p \leq 0.05$ by Duncan's multiple range test



$\text{Cu}(\text{OH})_3^-$, $\text{Cu}(\text{OH})_4^{2-}$, $\text{Cd}(\text{OH})^+$, $\text{Cd}(\text{OH})_2^{\circ}$, $\text{Cd}(\text{OH})_3^-$ and $\text{Cd}(\text{OH})_4^{2-}$ exist depending upon the solution pH [31], so that hydroxo-complexes are stable form of Cd^{2+} and Cu^{2+} ions. These two metals should be released from this stable form prior to be reduced by e_{aq}^- and H^{\cdot} . This led to lower removal percentages of Cu^{2+} and Cd^{2+} ions (≤ 5 and 10%, respectively) at high pH values as compared to those at low pH values (≥ 9 and 14%, respectively). On the other hand, easier reduction of Cu^{2+} ion in acidic solution and absorbed doses is considerable. This is ascribed to the higher reductive potential of Cu^{2+} ($\phi_{\text{Cu}^{2+}/\text{Cu}}^{\theta} = +0.340$ V and $\phi_{\text{Cu}^{2+}/\text{Cu}^+}^{\theta} = +0.159$ V) and Cu^+ ($\phi_{\text{Cu}^+/\text{Cu}}^{\theta} = +0.520$) as compared to Cd^{2+} ($\phi_{\text{Cd}^{2+}/\text{Cd}}^{\theta} = -0.403$ V) at the same concentration and pH value, which can be characterized by the reduction potentials of their metallic couples based on normal hydrogen electrode as the reference electrode [32].

Furthermore, as indicated in Table 1, effluent used in this study has some inorganic anions and cations, etc., which can react with reactive chemical species formed during irradiation, decreasing availability of these species to reach target pollutant and would accelerate or decelerate the removal depending on the type of pollutants [14]. In other words, the removal rate of pollutant may largely be influenced by physicochemical properties of background matrix. In particular, it was found that the percentage removal of metal in this research was lower than other studies conducted in Milli-Q water [17]. In addition, it is well known that inorganic ions such as CO_3^{2-} , HCO_3^- , NO_3^- , NO_2^- and SO_4^{2-} and dissolve oxygen and residue dissolved organic substances, and are commonly detected in the treated effluent [24] might compete with the target pollutant for reactive species [14]. Guo et al. [17] concluded that existence of organic carbon in water resources could decelerate the removal of heavy metals and it was gradually decreased with increasing gamma radiation dose. Therefore, it is expected that removal efficiency of heavy metals in wastewater was lower in the presence of anions that highly react with reducing species.

Mechanisms of heavy metals removal by TiO_2 NPs, MeOH and gamma irradiation

Generally, in the metal–NP system, when TiO_2 NPs suspended in water are combined with irradiation, a gamma ray can be directly absorbed by them. In this process, electron–hole pairs are radio-generated on the surface of the semiconductor by valence band (VB) electrons leaving holes (h_{vb}^+) and promoted to the conduction band (CB) (e_{cb}^-). The holes and electrons can either undergo direct recombination or diffuse separately to the surface of the NPs, where the holes react with adsorbed water or hydroxyl groups to

form adsorbed OH^{\cdot} and H^+ . These OH^{\cdot} radicals can combine to form H_2O_2 or they can attack the solute to produce intermediates and end products. Moreover, the electrons can be donated to oxygen to form superoxide radical which can enter into a chain reaction to produce H_2O_2 and HO_2^{\cdot} (Fig. 4) [16].

In addition, with addition of reductant to the metal–NP system, reductant scavenger oxidizing agent and accept holes, and subsequently, accelerate the radiocatalytic reduction of metal ions [5]. The destruction and mineralization of reductant in the metal–reductant– TiO_2 NP system related to the absorbed dose [13] and it could form CO_2 and H_2O (completely mineralized form) and formic acid (HCOOH), formate (HCOO^-), formaldehyde (CH_2O) and methoxy group (CH_3O^-) (incompletely mineralized form) [33].

Effects of TiO_2 NPs, MeOH and pH on Cu^{2+} and Cd^{2+} ions removal by gamma irradiation

According to Fig. 2a, it can be concluded that under different absorbed doses (gamma irradiation levels) addition of TiO_2 NPs had no significant effect on the removal of Cu^{2+} , but Cd^{2+} could be effectively removed. In basic solutions (Fig. 3a, b), the results differed from acidic solutions and TiO_2 NPs had significant effect on removal of both Cu^{2+} and Cd^{2+} ions but due to removal of the most Cu^{2+} and Cd^{2+} ions by precipitation in pH 9.0 and 12 and considering physical adsorption from the other side, the effect of irradiation on metal removal in basic solutions was negligible and was less than 5% of total removal. Thus, due to the results' uncertainty and negligible removal in pH 9.0 and 12 by irradiation, further discussion is done about results of the acidic solution in the following.

Radiocatalytic degradation efficiency of metals using TiO_2 NPs is affected by the solution pH. The surface charge of TiO_2 radiocatalysis is related to the IEP (isoelectric point or point of zero charges) and variation of suspension pH. In acidic (under isoelectric point) and alkaline (over isoelectric point) conditions, the titania surface can be positively or negatively charged by protonation or deprotonation, respectively [25]. In the case of TiO_2 Degussa P25 NPs, the isoelectric point is approximately 6.25 as introduced by the manufacturer and is consistent with those reported in other studies [25, 34]. Hence, the particle surface of TiO_2 NPs at pH value below and above 6.25 is positively and negatively charged by protonation or deprotonation, respectively. However, in lower and over IEP of TiO_2 NPs, the NP surface and occurrence form of metals have the similar charge. Due to repulsion forces of chemical metallic species and particle surface, it is unable to directly interact with the particle surface. Thus, because of the occurrence of the radio-catalytic reduction on the surface of the catalyst rather than in the bulk solution [18], the effect of TiO_2 NPs on



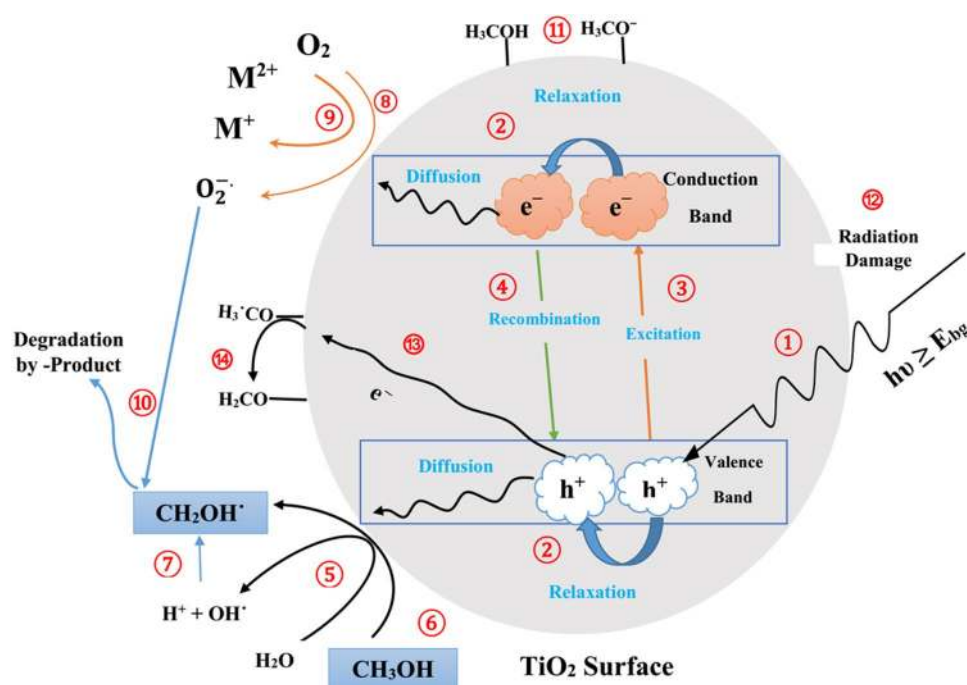


Fig. 4 Schematic illustration on removal of metal (M^{2+}) by the formation of radio-induced charge carriers (e^-/h^+) [16] and methanol oxidation adsorption [30] on semiconductor TiO_2 particle surfaces by gamma ray. (1) Excitation source (gamma ray) (2) radio-generated charges migrate to the catalyst surface (3) radio-generated electrons leaving holes (h^+) and promoted to conduction band (e^-) (4) electron-hole recombination (5) reaction of radio-induced hole with adsorbed water molecules to produce adsorbed OH^- and H^+ (6) scav-

enged radio-excited holes by methanol (7) scavenged adsorbed OH^- and H^+ by methanol (8) reaction of e^- with O_2 to produce superoxide radical (9) radio-catalytic reduction of dissolved metal ions to lower valence state with capturing of radio-generated e^- (10) reaction of superoxide radical with the added methanol to form other species (11) methanol and methoxy species adsorption to TiO_2 NPs (12) radiation-induced damage in the catalyst surface (13) secondary electrons (14) methoxy radical to formaldehyde and/or formate conversion

the removal of Cu^{2+} ion by gamma-ray treatment was not found to be pronounced, only a little more efficient at a 2 g L^{-1} TiO_2 concentration than in the absence of it under the same absorbed dose. On the other hand, it is well known that strong tendency to settlement and aggregation of TiO_2 NPs have an impact on nanoparticle adsorption and reactivity, so that aggregation and settlement would lead to the decrease in active surface area and radiocatalytic activity [35]. Thus, to ensure effective contact of the TiO_2 NPs and target pollutant, suspensions required continuous stirring to preventing catalyst settlement and aggregation [36]. The decreasing surface catalyst by settlement and aggregation and repulsion forces existing between the sorbent surface and chemical species may explain no significant effects of TiO_2 NPs on Cu^{2+} ion removal.

Moreover, radiocatalytic reduction of dissolved metal to zero valence state with capturing of radio-generated CB electron depending on the redox chemical species [19]. Therefore, for radio-reduction or radio-oxidation of a chemical species, the CB or VB of the semiconductor must be more negative or positive than the reduction or oxidation potential of the chemical species, respectively. As shown in Eqs. 5 and 6, the redox potentials of CB and VB are pH

dependent and the increase of solution pH makes the redox of CB and VB to shift to more cathodic potentials by 59 mV per pH unit. Thus, it could be one reason for removal of metals by irradiation at high pH values. On the other hand, unlike Cu^{2+} , the Cd^{2+} reduction potential is more negative than the radio-generated CB electrons, thus it cannot be reduced thermodynamically by CB electrons [18]. It is necessary to mention that although thermodynamical reduction of Cd^{2+} ion by nanoparticle is not feasible but significant removal of that by combination of nanoparticle and gamma irradiation could be attributed to its strong physical adsorption on the radiocatalyst.

In addition, Figs. 2a, b and 3a–d show the Cu^{2+} and Cd^{2+} ions removal increment by increasing irradiation dose in the presence of MeOH and TiO_2 NPs and in different initial pH values. Regardless of high pH values due to precipitation, it is found that Cu^{2+} and Cd^{2+} ions could be effectively removed by integrated application of MeOH and TiO_2 NPs as compared with their solus applications at the same absorbed doses. The highest Cu^{2+} and Cd^{2+} ions removals were attained when 10 kGy gamma ray + MeOH + TiO_2 NPs was used as compared with the other treatments. Generally, for radiocatalytic removal of heavy metals from wastewater,



the metal–reductant–TiO₂ NP coexisted systems must be more efficient than metal–TiO₂ NP system [5]. Although the metal–reductant–TiO₂ NP system in some cases has been studied [5, 18, 19] but it is not yet well understood with and without gamma-ray and MeOH treatment. However, due to decreasing oxygen concentration via oxygen-consuming reactions during irradiation, the oxygen-free conditions could take place in solution, especially using higher absorbed doses [37]. On the other hand, with taking into account MeOH destruction and mineralization related to the absorbed dose [13], the predominant indirect radio-oxidation of MeOH in the presence of water [38], protonation and deprotonation of nanoparticle [25] and MeOH with changing pH, the radiocatalytic oxidation of MeOH depends on the absorbed dose, solution pH, the presence of water and the concentration of O₂. Kongmany et al. [13] reported that at 1 kGy absorbed dose, the most of 1% by volume MeOH molecules would be destroyed and mineralized to CO₂ and H₂O. It is noteworthy that the addition of methanol (10% by volume) in 5 kGy is sufficient for scavenging oxidizing agent, but it is not completely mineralized to CO₂ and H₂O, as a result, it could form, HCOOH, HCOO[−], CH₂O and CH₃O[−] as primary intermediates. HCOO[−] and CH₂O intermediates are viewed as the primary products of direct and indirect oxidation reactions [30] and in the presence and absence of O₂ [33], respectively. However, with considering MeOH and primary intermediates deprotonation in the high pH values, the HCOO[−], CH₃O[−] and CH₂O could be formed at high pH in the 5 and 10 kGy levels and eventually yield CO₂ and H₂O. Wang et al. [38] reported that MeOH adsorbs to TiO₂ NPs into two adsorption mode: physisorbed as molecular CH₃OH (mobile) and chemisorbed as a CH₃O[−] (relatively stable). In the presence of water, CH₃OH/CH₃O[−] is involved in a reversible hydroxylation/dehydroxylation at the TiO₂ NPs surface. In addition, many previous studies showed that the CH₃O[−] produces more favorable hole-trapping sites than CH₃OH at room temperature, thereby prolonging the lifetime of CB electrons [26, 30]. On the other hand, at the metal–MeOH–acidic solution system, in addition to scavenging oxidizing species by MeOH, the acidic intermediate of MeOH such as HCOOH could combine with metal ions and affects its removal from wastewater [5]. However, at the higher absorbed dose (20 kGy) in lower and higher pH values, MeOH may be mineralized and would not supply better scavenging oxidizing species and hole acceptor.

G-value of metal ions removal from aqueous solutions under different conditions

G-values for Cu²⁺ and Cd²⁺ ions removal from aqueous solutions under different conditions are compared in Table 3. This table shows that, in general, G-values were increased

by increment of the solution pH in order of pH 12 > pH 9.0 > pH 4.5 regardless of the type of the treatment, showing that Cu²⁺ and Cd²⁺ ions removal processes are more effective under the solution pH 12 conditions. This result could be attributed to precipitation (not irradiation effect) and its role on metal removal.

However, the results showed that the G-value was decreased with the increase of absorbed dose in both acidic and basic solutions in the same treatments (Table 2). According to this result, efficiency of the gamma irradiation process decreases with longer gamma exposure time. This trend can be attributed to (1) the recombination reactions of radical–radical, (2) the competitive for solute molecules between the reactive radicals and (3) the competitive reactions for radicals between the solute and reaction by-product [15, 39]; thus, the radical concentration for reaction with Cu²⁺ and Cd²⁺ ions reduced. Although the G-values were increased with adding TiO₂ NPs and/or MeOH separately and in combination, the increasing amount in acidic condition was greater than the basic condition and the highest value was attained from the 5 kGy gamma dose + MeOH + TiO₂ NPs for both Cu²⁺ and Cd²⁺ ions (Table 2). Therefore, it can be assumed that e_{aq}^- and H[•] radicals produced in the presence of additive may remove Cu²⁺ and Cd²⁺ ions more effectively. The reasons may include the following: a stronger OH[•] scavenger compared to e_{aq}^- and H[•] and donating the electron to radio-excited holes by MeOH and radio generation of the electron from CB of TiO₂ NPs. The radiation chemical yield trend reported here is consistent with published findings for radiolytic degradation of Cd²⁺ and Pb²⁺ ions in the presence of sodium carbonate as scavenger OH[•] radical [17].

Overall, it should be mentioned that according to the G-value equation, the subtraction between solute concentration before and after irradiation is located in the numerator and absorbed dose in the denominator. The denominator of the G-value equation cannot be zero. The G-value cannot be calculated for removal of Cu²⁺ and Cd²⁺ ions under different additions of pH, methanol and TiO₂ NPs in without irradiation treatments (the denominator cannot be zero). Thus, due to the inability to eliminate the effects of physical adsorption and precipitation of metals ion in the G-value equation, its values are far from reality in mentioned condition. Therefore, the G-value content is not recommended for comparing the efficiency of the irradiation in basic solution or under radiocatalysis condition.

Dose required for 90 and 99 percentages of metal ions removal from aqueous solutions under different conditions

According to the concentrations of some primary active species calculated from G-values given for Eq. 1 [(target pollutant) ≤ (active species)], it has been found that the relation



Table 2 G-values of Cd²⁺ and Cu²⁺ ions removal under different conditions

Treatments			G-value ($\times 10^{-7} \text{ mol j}^{-1}$) [*]					
			Acidic solution (pH 4.5)		Basic solution			
Absorbed dose (kGy)	Methanol (% <i>, v/v</i>)	TiO ₂ nanoparticle (g L ⁻¹)	Cu ²⁺	Cd ²⁺	pH 9.0		pH 12	
					Cu ²⁺	Cd ²⁺	Cu ²⁺	Cd ²⁺
5	0	0	0.27 ± 0.01ef	0.18 ± 0.02gh	1.85 ± 0.00e	1.80 ± 0.00e	1.88 ± 0.00c	1.89 ± 0.00b
5	0	2	0.31 ± 0.02e	0.28 ± 0.00e	1.87 ± 0.00d	1.82 ± 0.00e	1.89 ± 0.00b	1.89 ± 0.00b
5	10	0	0.67 ± 0.03c	0.51 ± 0.00c	1.88 ± 0.00cd	1.83 ± 0.00d	1.89 ± 0.00b	1.91 ± 0.00a
5	10	2	0.99 ± 0.01a	0.90 ± 0.01a	1.88 ± 0.00c	1.87 ± 0.00c	1.90 ± 0.00a	1.91 ± 0.00a
10	0	0	0.21 ± 0.01gh	0.14 ± 0.00ij	0.93 ± 0.00h	0.92 ± 0.00k	0.95 ± 0.00f	0.95 ± 0.00h
10	0	2	0.23 ± 0.00fg	0.20 ± 0.00g	0.94 ± 0.00g	0.93 ± 0.00j	0.95 ± 0.00f	0.95 ± 0.00h
10	10	0	0.53 ± 0.00d	0.40 ± 0.00d	0.94 ± 0.00f	0.93 ± 0.00j	0.95 ± 0.00f	0.95 ± 0.00h
10	10	2	0.73 ± 0.01b	0.59 ± 0.00b	0.95 ± 0.00f	0.94 ± 0.00i	0.95 ± 0.00f	0.96 ± 0.00g
20	0	0	0.17 ± 0.00h	0.12 ± 0.00j	0.47 ± 0.00j	0.46 ± 0.00n	0.48 ± 0.00i	0.48 ± 0.00i
20	0	2	0.18 ± 0.00h	0.15 ± 0.00i	0.47 ± 0.00j	0.47 ± 0.00m	0.48 ± 0.00i	0.48 ± 0.00i
20	10	0	0.18 ± 0.00gh	0.16 ± 0.00hi	0.47 ± 0.00j	0.47 ± 0.00m	0.48 ± 0.00i	0.48 ± 0.00i
20	10	2	0.28 ± 0.00ef	0.25 ± 0.00f	0.48 ± 0.00i	0.47 ± 0.00m	0.48 ± 0.00i	0.48 ± 0.00i

Different letters in acidic (pH 4.5) and basic (pH 9 and 12) solution for each metals show significant difference at $p \leq 0.05$ by Duncan's multiple range test

^{*}Calculated from Eq. 7

between the removal of Cu²⁺ and Cd²⁺ ions in the solution and the absorbed dose is well subject to the first order kinetics model, which is described as follow [5]:

$$C = C_0 e^{-K_1 D}, \quad (15)$$

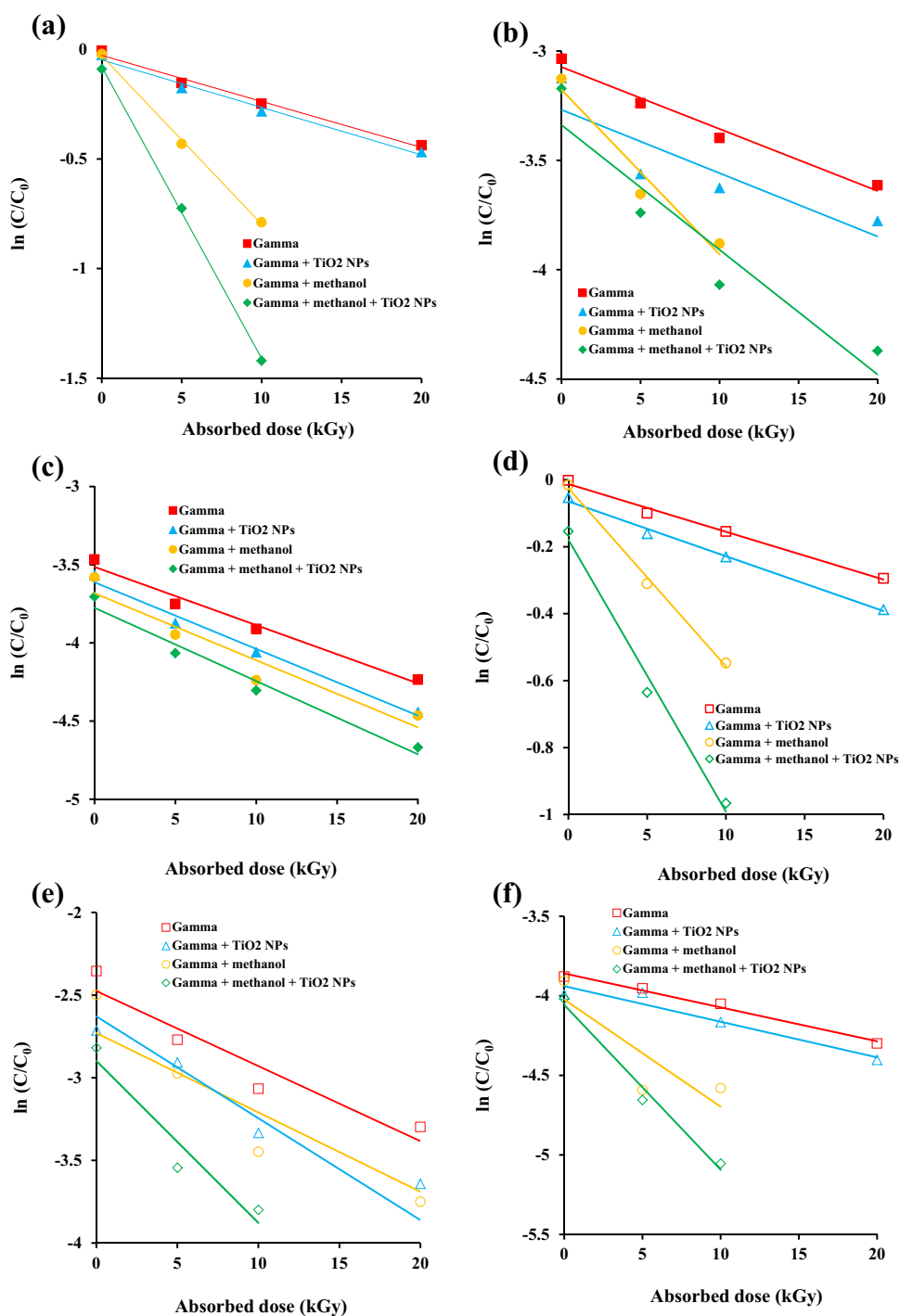
$$\ln \left(\frac{C}{C_0} \right) = -K_1 D. \quad (16)$$

The linearization of the exponential Eq. 15 by natural logarithm (Eq. 16) gives straight line and slope of this straight line would be the dose constant “K₁”. Where C₀ is the initial concentration of the Cu²⁺ and Cd²⁺ ions before irradiation (mol L⁻¹), C is the concentration of the Cu²⁺ and Cd²⁺ ions at any applied dose (mol L⁻¹), D is the absorbed dose (kGy), and K₁ is the rate constant or dose constant (kGy⁻¹). As shown in Fig. 5a–f, the experimental data were better fitted and linearized with minimum error (more r²) according to Eq. 16 (Table 3); for reduction of Cu²⁺ and Cd²⁺ ions in solutions under different conditions on the entire dose range, except for some treatments, i.e., gamma + MeOH, gamma + MeOH + TiO₂ NPs at pH 4.5 for both Cu²⁺ and Cd²⁺ ions (Fig. 5a and d, respectively), gamma + MeOH + TiO₂ NPs at pH 9.0 for Cd²⁺ ion (Fig. 5e), gamma + MeOH and gamma + MeOH + TiO₂ NPs at pH 12 for Cd²⁺ ion (Fig. 5f) when the absorbed dose was less than 10 kGy. Based on the K₁ at different conditions, D_{0,9} and D_{0,99}, the required doses to reduce 90 and 99% of initial concentration are shown in Table 3. At any applied pH, in

the presence of TiO₂ NPs and MeOH either separately or in combination, dose constant has relatively higher values, so that higher increase was observed in MeOH alone application or in combination with TiO₂ NPs (Table 3). This shows that Cu²⁺ and Cd²⁺ ions can be removed at a faster rate with MeOH addition in separately or in combination with TiO₂ NPs.

In addition, our results showed that D_{0,9} and D_{0,99} for removal of Cu²⁺ and Cd²⁺ ions were decreased with the addition of MeOH and TiO₂ NPs in separately and in combination for all pH levels; so that the highest reduction in required absorbed dose for complete removal of metal ions from the solution was obtained by integrated application of MeOH and TiO₂ NPs (Table 3). This could be used as a tool for comparison of the radiolysis-based experiments. Thus, it can be distinguished from Table 3 that in the presence of MeOH + TiO₂ NPs, the applied gamma irradiation doses to remove 99% of Cu²⁺ and Cd²⁺ ions were decreased from 218 to 34 and 321 to 56 kGy at pH 4.5, from 162 to 80 and 101 to 46 kGy at pH 9.0 and from 123 to 98 and 215 to 44 kGy at pH 12, respectively, in comparison with absence of both MeOH and TiO₂ NPs. This further indicates that the integrated application of MeOH and TiO₂ NPs at low pH value is favorable for complete removal of coexisting Cu²⁺ and Cd²⁺ ions. This could be attributed to MeOH role as scavenger [39], electron production due to gamma irradiation of TiO₂ NPs [14], occurrence forms of contaminants [17] and reactive species generated during water radiolysis [14].

Fig. 5 Effects of gamma, gamma + TiO₂ NPs, gamma + methanol and gamma + methanol + TiO₂ NPs treatments on removal kinetics of Cu²⁺ (a–c) and Cd²⁺ (d–f) at pH 4.5 (a and d), pH 9.0 (b and e) and pH 12 (c and f)



Similar results were also reported by other researchers for different additives in water [12] and wastewater [5].

Limitations and research aspects for the future

At the end, ionizing radiation technique could be regarded as rapid method for heavy metal removal and the time consuming to remove metals depends on specific activity of isotopic sources for gamma irradiation and/or energy and

power of machine generated ionizing radiation (electron beam) [40]. Although there are some environmental concerns such as waste material (sludge) and/or by-product generated by the system and the possible post-treatment required, initial capital cost and affordable the proposed system compared with the conventional methods, the successful use of the system to remove other metal ions, possible to directly integrate the system developed in this study to conventional sewage treatment facilities, etc. It



Table 3 Doses required for 90 ($D_{0.9}$) and 99% ($D_{0.99}$) removal of 1 mM Cd^{2+} and Cu^{2+} ions with increasing absorbed dose

Systems	r^{2*}		Dose constant K_1 (kGy^{-1}) ⁺		$D_{0.9}$ (kGy)		$D_{0.99}$ (kGy)	
	Cu^{2+}	Cd^{2+}	Cu^{2+}	Cd^{2+}	Cu^{2+}	Cd^{2+}	Cu^{2+}	Cd^{2+}
pH 4.5, gamma	0.988	0.991	0.021	0.0143	109.65	161.02	218.82	321.34
pH 9, gamma	0.975	0.908	0.0283	0.0454	81.36	50.72	162.37	101.21
pH 12, gamma	0.980	0.987	0.0372	0.0213	61.90	108.10	123.52	215.73
pH 4.5, gamma + TiO_2 NPs	0.986	0.993	0.0217	0.0164	106.11	140.40	211.76	280.19
pH 9, gamma + TiO_2 NPs	0.776	0.958	0.029	0.048	79.40	47.97	158.45	95.73
pH 12, gamma + TiO_2 NPs	0.986	0.931	0.0426	0.0224	54.05	102.79	107.87	205.14
pH 4.5, gamma + methanol	0.998	0.996	0.0768	0.0532	29.98	43.28	59.83	86.37
pH 9, gamma + methanol	0.949	0.920	0.0753	0.0616	30.58	37.38	61.02	74.60
pH 12, gamma + methanol	0.920	0.738	0.0429	0.0673	53.67	34.21	107.11	68.28
pH 4.5, gamma + methanol + TiO_2 NPs	0.999	0.988	0.133	0.0813	17.31	28.32	34.55	56.52
pH 9, gamma + methanol + TiO_2 NPs	0.90	0.928	0.0571	0.0979	40.33	23.52	80.47	46.94
pH 12, gamma + methanol + TiO_2 NPs	0.972	0.982	0.0468	0.1036	49.20	22.23	98.19	44.35

* r^2 of the linearization of the data by natural logarithm in the studied systems

⁺Obtained from the slope of linearized equation by natural logarithm

is evident from the literature survey that (1) there is very low data regarding initial capital cost, successful implementation, affordable and directly integrate system (ionizing radiation process) to conventional sewage treatment facilities for heavy metal decontamination of effluent and strongly required to be further explored. However, it is well-established that to realize a process utilizing ionizing radiation, the electron beam accelerator and not gamma irradiation would employ cost-effective in commercial plant [11], but it should be noted that isotopes are convenient and uncomplicated sources of radiation and by far, most experimental works have been done using isotope gamma-ray sources and most of the comments made gamma ray are equally applicable to other sources of ionizing radiation [40]. (2) Using ionizing radiation in combination with NPs and/or reductant (MeOH) has some limitations such as produced sludge and unknown byproducts. Major part of produced sludge is radiocatalyst particle, thus separation of catalyst particles from the treated effluent is necessary and coupling of the radiocatalysis with membrane technology seems hopeful [41]. In addition, the use of TiO_2 thin films rather than suspended form (particle) could be proposed for investigation in future studies. So that, thin film application obviously overcomes the disadvantage of separate catalyst from liquid at the end of the experimental period [36]. Unknown byproducts especially at low absorbed dose are likely to be raised as an environmental concern and strongly required to be further explored by pulse radiolysis and other modern analytical techniques including liquid chromatography–mass spectrometry, gas chromatography–mass spectrometry, ion chromatography, etc. (3) From other metal ions removal standpoint, which have physicochemical

properties different from those of Cu^{2+} and Cd^{2+} ions, it could be mentioned that the potential removal ability varies from one metal ion to another and is related to many factors, such as reductive potential, hydrated ionic radius and hydration energy of the metals. [28].

Conclusions

In basic solutions (pH of 9.0 and 12), the main reason for Cu^{2+} and Cd^{2+} ions removal was precipitation as hydroxo-complexes ($\geq 90\%$ and 95% , respectively), so that removals by physical adsorption and gamma irradiation with and without MeOH and TiO_2 NPs additions were negligible with a total of less than 10%. In acidic solution (pH 4.5), gamma irradiation is proved to be an efficient method for removing Cu^{2+} and Cd^{2+} ions from wastewater. Cd^{2+} had high physical adsorption capacity on the TiO_2 NPs, but Cu^{2+} had higher removal percentage by gamma irradiation at the same experimental conditions. The removal kinetics of Cu^{2+} and Cd^{2+} ions by reducing species under different conditions could be described by the first order kinetic equation. The removal efficiency was dependent on the absorbed dose, pH and presence of MeOH and TiO_2 NPs. Removal of Cu^{2+} and Cd^{2+} ions was facilitated in low pH conditions and combined using of MeOH and TiO_2 NPs. The complete removal was achieved using an absorbed dose about 50 kGy with combined application of MeOH and TiO_2 NPs in acidic solution. At any applied solution pH, the dose constant has relatively greater values for the studied metal ions in the combined TiO_2 NPs and MeOH treatments and was about six times greater than that of without these additives in acidic solution.

Compliance with ethical standards

Conflict of interest The authors declare they have no conflict of interests.

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References

- Berni, R., Luyckx, M., Xu, X., Legay, S., Sergeant, K., Hausman, J.F., Lutts, S., Cai, G., Guerriero, G.: Reactive oxygen species and heavy metal stress in plants: impact on the cell wall and secondary metabolism. *Environ. Exp. Bot.* (2018). <https://doi.org/10.1016/j.envexpbot.2018.10.017>
- Asgari Lajayer, B., Ghorbanpour, M., Nikabadi, S.: Heavy metals in contaminated environment: destiny of secondary metabolite biosynthesis, oxidative status and phytoextraction in medicinal plants. *Ecotoxicol. Environ. Saf.* **145**, 377–390 (2017)
- Pawar, R.R., Kim, M., Kim, J.G., Hong, S.M., Sawant, S.Y., Lee, S.M.: Efficient removal of hazardous lead, cadmium, and arsenic from aqueous environment by iron oxide modified clay-activated carbon composite beads. *Appl. Clay Sci.* **162**, 339–350 (2018)
- Edelstein, M., Ben-Hur, M.: Heavy metals and metalloids: sources, risks and strategies to reduce their accumulation in horticultural crops. *Sci. Hortic.* **234**, 431–444 (2018)
- Zaki, A., El-Gendy, N.A.: Removal of metal ions from wastewater using EB irradiation in combination with HA/TiO₂/UV treatment. *J. Hazard. Mater.* **271**, 275–282 (2014)
- Fu, F., Wang, Q.: Removal of heavy metal ions from wastewaters: a review. *J. Environ. Manag.* **92**, 407–418 (2011)
- Gu, P., Zhang, S., Li, X., Wang, X., Wen, T., Jehan, R., Alsaedi, A., Hayat, T., Wang, X.: Recent advances in layered double hydroxide-based nanomaterials for the removal of radionuclides from aqueous solution. *Environ. Pollut.* **240**, 493–505 (2018)
- Li, J., Wang, X., Zhao, G., Chen, C., Chai, Z., Alsaedi, A., Hayat, T., Wang, X.: Metal-organic framework-based materials: superior adsorbents for the capture of toxic and radioactive metal ions. *Chem. Soc. Rev.* **47**, 2322–2356 (2018)
- Yu, S., Wang, X., Pang, H., Zhang, R., Song, W., Fu, D., Hayat, T., Wang, X.: Boron nitride-based materials for the removal of pollutants from aqueous solutions: a review. *Chem. Eng. J.* **333**, 343–360 (2018)
- Zhao, G., Huang, X., Tang, Z., Huang, Q., Niu, F., Wang, X.K.: Polymer-based nanocomposites for heavy metal ions removal from aqueous solution: a review. *Polym. Chem.* **9**, 3562–3582 (2018)
- Han, B., Kim, J.K., Kim, Y., Choi, J.S., Jeong, K.Y.: Operation of industrial-scale electron beam wastewater treatment plant. *Radiat. Phys. Chem.* **81**, 1475–1478 (2012)
- Chaychian, M., Al-Sheikhly, M., Silverman, J., McLaughlin, W.L.: The mechanisms of removal of heavy metals from water by ionizing radiation. *Radiat. Phys. Chem.* **53**, 145–150 (1998)
- Kongmany, S., Furuta, M., Matsuura, H., Okuda, S., Imamura, K., Maeda, Y.: Degradation of phorbol 12, 13-diacetate in aqueous solution by gamma irradiation. *Radiat. Phys. Chem.* **105**, 98–103 (2014)
- Wang, J., Chu, L.: Irradiation treatment of pharmaceutical and personal care products (PPCPs) in water and wastewater: an overview. *Radiat. Phys. Chem.* **125**, 56–64 (2016)
- Changotra, R., Guin, J.P., Khader, S.A., Varshney, L., Dhir, A.: Electron beam induced degradation of ofloxacin in aqueous solution: kinetics, removal mechanism and cytotoxicity assessment. *Chem. Eng. J.* **356**, 973–984 (2019)
- Yu, S., Hu, J., Wang, J.: Radiation-induced catalytic degradation of p-nitrophenol (PNP) in the presence of TiO₂ nanoparticles. *Radiat. Phys. Chem.* **79**, 1039–1046 (2010)
- Guo, Z., Tang, D., Liu, X., Zheng, Z.: Gamma irradiation-induced Cd²⁺ and Pb²⁺ removal from different kinds of water. *Radiat. Phys. Chem.* **77**, 1021–1026 (2008)
- Chen, D., Ray, A.K.: Removal of toxic metal ions from wastewater by semiconductor photocatalysis. *Chem. Eng. Sci.* **56**, 1561–1570 (2001)
- Khalil, L., Rophael, M., Mourad, W.: The removal of the toxic Hg(II) salts from water by photocatalysis. *Appl. Catal. B. Environ.* **36**, 125–130 (2002)
- González-Juárez, J., Jiménez-Becerril, J., Carrasco-Ábregob, H.: TiO₂, Al₂O₃ and SiO₂ as radiocatalyst ceramics. *J. Ceram. Process. Res.* **10**, 534–535 (2009)
- Kang, S.W., Shim, S.B., Yoo, J., Jung, J.: Effect of titanium dioxide nanoparticles on gamma-ray treatment of phenol in different matrices: implications in toxicity toward *Daphnia magna*. *Bull. Environ. Contam. Toxicol.* **89**, 893–897 (2012)
- Li, Y., Li, L., Chen, Z.X., Zhang, J., Gong, L., Wang, Y.X., Zhao, H.Q., Mu, Y.: Carbonate-activated hydrogen peroxide oxidation process for azo dye decolorization: process, kinetics, and mechanisms. *Chemosphere* **192**, 372–378 (2018)
- Wasim, M.A., Ullah, R., AbdEl-Salam, N.M., Ayaz, S.: Gamma radiation induced decolorization of an aqueous textile dye solution in the presence of different additives. *Desalin. Water. Treat.* **55**, 1945–1955 (2015)
- APHA: The standard methods for the examination of water and wastewater, 20th edn. American Public Health Association, Washington (1998)
- Andronic, L., Perniu, D., Duta, A.: Synergistic effect between TiO₂ sol-gel and degussa P25 in dye photodegradation. *J. Sol-Gel Sci. Technol.* **66**, 472–480 (2013)
- Zhao, J., Yang, J., Petek, H.: Theoretical study of the molecular and electronic structure of methanol on a TiO₂ (110) surface. *Phys. Rev. B.* **80**, 235416 (2009)
- Ripin, D.H., Evans, D.A.: pK_a's of inorganic and oxo-acids. *Chem* **206**. http://ccc.chem.pitt.edu/wipf/MechOMs/evans_pKa_table.pdf. Accessed 16 Feb 2015
- Nassar, N.N.: Rapid removal and recovery of Pb(II) from wastewater by magnetic nanoadsorbents. *J. Hazard. Mater.* **184**, 538–546 (2010)
- Lv, L., Hor, M.P., Su, F., Zhao, X.: Competitive adsorption of Pb²⁺, Cu²⁺, and Cd²⁺ ions on microporous titanosilicate ETS-10. *J. Colloid Interface Sci.* **287**, 178–184 (2005)
- Panayotov, D.A., Burrows, S.P., Morris, J.R.: Photooxidation mechanism of methanol on rutile TiO₂ nanoparticles. *J. Phys. Chem. C* **116**, 6623–6635 (2012)
- Bodek, I.: Environmental inorganic chemistry: properties, processes, and estimation methods. Pergamon Press, New York (1988)
- Speight, J.G.: Lange's handbook of chemistry. McGraw-Hill, New York (2005)
- Henderson, M.A.: A surface science perspective on photocatalysis. *Surf. Sci. Rep.* **66**, 185–297 (2011)
- Ong, S.T.: Application of experimental design for dyes removal in aqueous environment using sodium alginate-TiO₂ thin film. *Chem. Data. Coll.* **15**, 32–40 (2018)



35. Pettibone, J.M., Cwiertny, D.M., Scherer, M., Grassian, V.H.: Adsorption of organic acids on TiO₂ nanoparticles: effects of pH, nanoparticle size, and nanoparticle aggregation. *Langmuir* **24**, 6659–6667 (2008)
36. McCullagh, C., Robertson, J.M., Bahnemann, D.W., Robertson, P.K.: The application of TiO₂ photocatalysis for disinfection of water contaminated with pathogenic micro-organisms: a review. *Res. Chem. Intermed.* **33**, 359–375 (2007)
37. Chu, L., Yu, S., Wang, J.: Degradation of pyridine and quinoline in aqueous solution by gamma radiation. *Radiat. Phys. Chem.* **144**, 322–328 (2018)
38. Wang, C.Y., Groenzin, H., Shultz, M.J.: Comparative study of acetic acid, methanol, and water adsorbed on anatase TiO₂ probed by sum frequency generation spectroscopy. *J. Am. Chem. Soc.* **127**, 9736–9744 (2005)
39. Wang, J., Zhuan, R., Chu, L.: The occurrence, distribution and degradation of antibiotics by ionizing radiation: an overview. *Sci. Total Environ.* **646**, 1385–1397 (2019)
40. Tarr, M.A.: *Chemical degradation methods for wastes and pollutants: environmental and industrial applications*. CRC Press, New Orleans (2003)
41. Bet-moushoul, E., Mansourpanah, Y., Farhadi, K., Tabatabaei, M.: TiO₂ nanocomposite based polymeric membranes: a review on performance improvement for various applications in chemical engineering processes. *Chem. Eng. J.* **283**, 29–46 (2016)

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