

Removal of Toxic Metal Ions in Water by Photocatalytic Method

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Authors' contributions

This work was carried out in collaboration between all authors. Authors ETW and MM designed the study, managed the photoreaction study, and wrote the first draft of the manuscript. Author NHA managed the analyses of the study. Authors HH and AMW carried out the research and managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Aims: To study the photocatalytic method for decreasing the concentration of Cu(II), Cd(II), Cr(VI), and Pb(II) in the solutions.

Study Design: The photocatalytic process was proceeded for single solutions containing respective Cu(II), Cd(II), Cr(VI), and Pb(II) ions. Reaction time, photocatalyst dose, and solution pH were optimized. The influence of Cr(VI), Cd(II) and Pb(II) ions on the Cu(II) removal was also evaluated.

Place and Duration of Study: Laboratory of Analytical Chemistry, Chemistry Department, Gadjah Mada University, Indonesia. June 2013 – January 2014.

Methodology: Photocatalytic process was carried out by irradiating 100 ml of 4 single solutions containing 10 mg/L of Cu(II), Cd(II), Cr(VI) and Pb(II) added with TiO₂ with UV lamp having 290-390 nm of the wavelength, for certain time. The same procedure was also taken place with variation of photocatalyst dose (10, 25, 50, 75, and 100 mg for 100 ml solution), irradiation time (1,

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3, 5, 10, 25, 50, and 75 h), and solution pH (1, 3, 5, 7, 9, and 13), and for 3 solutions containing Cu(II), that was added with Cd(II), Cr(VI), and Pb(II) respectively. The concentrations of Cu(II), Cd(II) and Pb(II) ions in the solutions were measured by AA Spectrophotometer and by spectrophotometer UV-Visible for Cr(VI) ion.

Results: The maximum effectiveness of the photocatalytic process can be obtained by using 50 mg of TiO₂, in 24 h and at pH 5, that can take Cu(II), Cr(VI), Cd(II) and Pb(II) out from the solutions as high as 45.56%, 77.72%, 15.23%, and 40.32%, by photocatalytic reduction, adsorption on TiO₂ and photocatalytic oxidation, respectively. The presence of Cr(VI) and Cd(II) can decrease Cu(II) photo reduction from 45.36% into 15.24% and into 40.53%, meanwhile Pb(II) improves the photo reduction from 45.56 into 58.76% for low Pb(II) concentration.

Conclusion: The concentration of the toxic Cu(II) and Cr(VI), Cd(II), and Pb(II) ions can be successfully decreased by photocatalytic process through different mechanisms. The removal of the metal ions was controlled by photocatalyst dose, irradiation time, and solution pH. The presence of Cr(VI) and Cd(II) can inhibit Cu(II) photoreduction due to the competition, meanwhile Pb(II) with low concentration promotes Cu(II) photoreduction by synergic effect.

Keywords: Removal; Cu; Cr(VI); Cd; Pb; TiO₂ photocatalytic; photoreduction; photooxidation.

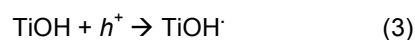
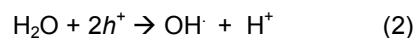
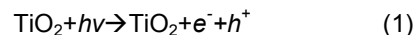
1. INTRODUCTION

Several heavy metal ions such as Cd(II), Cr(VI), Cu (II) and Pb(II) can be distributed in the environment from wastewater disposal of some industries including electroplating activities, paint, electric equipment, nylon and plastic factories. Since all metal ions are hazard for human and environment [1], efforts for removal the metal ions from wastewater have attracted much attention.

Removal of Cd(II), Cr(VI), Cu (II) and Pb(II) ions has been intensively studied by conventional adsorption method, i.e by using zeolite [2], activated carbon [3], and biomass [4]. This method is normally simple and effective, but it is unable detoxify the hazardous ions, except the method only transfers the ions from the solution into the solid adsorbent. In addition, when the adsorbent is saturated with the metal ions, it becomes a solid waste that lead to a further environmental problem. Hence, a treatment method which is able to remove as well as detoxify the hazardous ions is required. Such method may be satisfied by photocatalytic reduction-oxidation.

Photocatalytic reduction and photocatalytic oxidation are reduction and oxidation induced by photon or UV light and sensitized by photo catalyst such as TiO₂. This oxide can be functioned as a photo catalyst due to its semiconductor structure, that is a structure characterized by electron filled valence band and empty conduction band, separated by a gap called as band gap energy as much as 2-3.5 eV [5]. With such structure, when a semiconductor is

irradiated by UV or visible light, one electron in the valence band can be transferred into conduction band by leaving a hole symbolized as h^+ which is actually a positive radical. When the hole contacts with water and TiOH photocatalyst surface, OH radical is formed. The photo generation of electron and hole, and formation of OH radical are written as reactions (1), (2) and (3).



The OH radical can act as a strong oxidizing agent that has been tested for removing pesticides [6] and phenolic pollutants [7] through photodegradation, as well as Pb(II) [8] from the solutions through photooxidation mechanism. Meanwhile, the electron is widely used for reducing some metal ions, including Hg(II) [9,10] and Cr(VI) [11,12], as well as for Ag recovering from photography wastewater [13]. It was reported that hazardous Hg(II) and Cr(VI) could be successfully reduced into less or non toxic Hg(0) and Cr(III), respectively. Meanwhile, Ag(I) could be reduced into Ag(0) deposited on the photocatalyst surface, enabling it to be easily taken out as pure and valuable silver metal. Moreover, the study on photocatalytic reduction of Cu(II) in the presence of TiO₂ for removing the ion from its solution has also been reported [14,15]. However, a comparison study on the removal of Cu(II), Cr(VI), Cd(II) and Pb(II) ions by photocatalytic technology has not been explored yet. In the present paper, the removal of Cu(II),

Cr(VI), Cd(II) and Pb(II) ions by photocatalytic technology and the study on the influence Cr(VI), Cd(II) and Pb(II) with varying concentration and solution pH on the photoreduction of Cu (II) ion are reported.

2. METHODOLOGY

2.1 Materials and Instruments

TiO₂ powder, Cu(NO₃)₂·3H₂O, K₂Cr₂O₇, CdCl₂, Pb(NO₃)₂, HCl and NaOH pellet purchased from E.Merck, with analytical grade were used without further purification. The instruments used were a photoreaction apparatus having dimension of 50x150x 50 cm³, installed with UV Lamp and magnetic stirring plate as illustrated by Fig. 1, Perkin-Elmer atomic absorption spectrophotometer (AAS) for analyzing Cu, Cd, and Pb in the solutions and GBC Cintra 100 UV/Visible spectrophotometer to determine Cr(VI) ions in the solution.

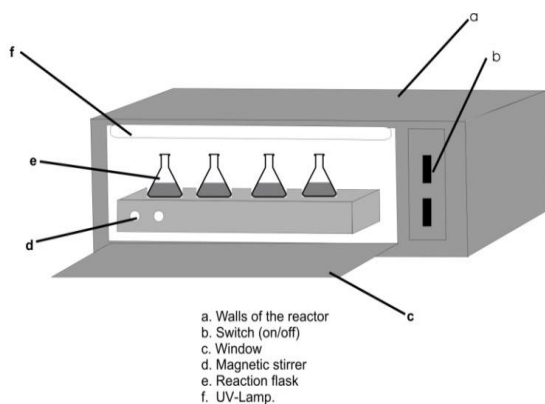


Fig. 1. The apparatus for photocatalytic experiment

2.2 Photocatalytic Experiment

Removal of Cu(II) in the solution was carried out in a closed reactor equipped with a 40 watt UV lamp having wave length in the range of 290-390 nm. For that purpose, 100 ml solution containing 10 mg/L, that is equal to 0.16 mmole of Cu(II) with alteration pH as designed, was mixed with 50 mg TiO₂, then the suspension was irradiated by UV light in the photoreaction apparatus for 24 h. The solution obtained by filtering the suspension, was analyzed by Perkin-Elmer AAS to determine the concentration of unreduced Cu(II) ions. By subtracting the initial and unreduced concentrations of the ions, the degree of Cu(II) photoreduction could be calculated. The

removal of Cr(VI), Cd(II) and Pb(II) as a single solute in the solution was performed by using the same procedure as carried out for Cu(II) removal. The influence of respective Cr(VI), Cd(II) and Pb(II) on the photoreduction catalytic of Cu(II) was performed by irradiating 3 serial suspension of Cu(II) solutions suspended with TiO₂ that was added by Cr(VI), Cd(II) and Pb(II) respectively. The next step is same as above.

3. RESULTS AND DISCUSSION

3.1 Removal of the Metal Ions by Photocatalytic Process Using TiO₂ Photocatalyst

The results of the photocatalytic process is illustrated by Fig. 2, indicating that the concentration of Cu(II), Cr(VI), Cd(II), and Pb(II) ions in the solution can be decreased. The most effective decreasing is found by Cr(VI), following by Cu(II), Pb(II), and Cd(II). The decrease of the concentration of Cr(VI) [11,12] and Cu(II) is caused by photocatalytic reduction [14,15]. The photoreduction of Cr(VI) and Cu(II) is generated by capturing the electrons released via photolysis of water and TiO₂ photocatalyst [3], as shown by reaction (1), (4), and (5):

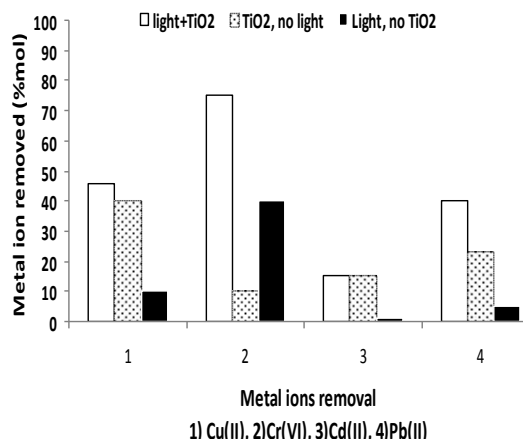
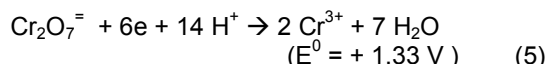
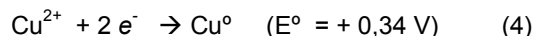
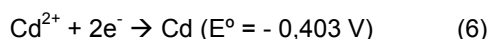


Fig. 2. Removal of Cu(II), Cr(VI), Cd(II) and Pb(II) ions in the various conditions of process

The effectiveness of the photocatalytic reduction of Cr(VI) is higher than that of Cu(II) which is consistence with their reduction potential values,

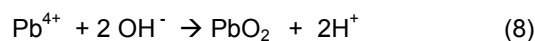
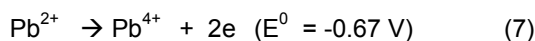
as written as reaction (4) and (5). The higher potential reduction represents the easiness of the ions to be reduced. Meanwhile in the dark process, decreasing concentration of Cr(VI) is lower than that of Cu(II) ion. In the dark condition, the removal is induced by adsorption on TiO₂ surface that provide negative charge as active sites and in such condition, a photoreduction is unlikely to be occurred. It is implied that the adsorption of Cu(II) as cationic on the surface of TiO₂ is favorable than an anionic CrO₄²⁻ of Cr(VI) ion. This fact can be understood, as known well that the negative sites prefer to attach the positive ion or cationic.

The lowest removal of Cd(II) from the solution by photocatalytic process is supposed to be caused by adsorption on the surface of TiO₂. Because Cd(II) cannot be reduced, as indicated by negative standard reduction potential (E°), as seen in reaction (6). The adsorption of Cd²⁺ takes place on the surface of TiO₂ that has more electrons.



The adsorption of Cd²⁺ is also supported by data obtained in the dark (no light) condition in the presence of TiO₂, showing that in such condition the concentration of Cd(II) goes down as much as in the lighted process. It is strongly proved that photoreduction or photooxidation of Cd(II) ions does not occur.

Meanwhile, by photocatalytic process, the declining concentration of Pb(II) may be due to photooxidation induced by positive radicals of h^{+} provided by TiO₂ photocatalyst. In the solution, Pb(II) ion exists as Pb²⁺ that is unlikely to be reduced but is possible to be oxidized into Pb(IV) formed as PbO₂ [8]. The photooxidation of Pb(II) is written as reaction (7) and (8), that also shows negative reduction potential value, indicating that the Pb(II) is not reducible ion, but it is oxidizable one. In addition, the low value of Pb(II) removal indicates that oxidation of Pb(II) ion takes place slowly, explaining the low decreasing Pb(II) concentration.



3.2 The Influence of Solution pH

The degree of metal ions removal at pH alteration is shown by Fig. 3. It is seen in the

figure that in the solution with increasing pH from 1-3, the removal degrees of all metals raise slightly, and sharp improvement is observed when the pH is increased up to 5. Increasing solution pH from 5 to 7, causes the degree of Cr(VI) removal sharply declined, while that of Cu(II), Cd(II) and Pb(II) enlarge drastically. Further increasing pH up to 14, makes the removal degree of Cr(VI) further decreased, meanwhile the removal degrees of Cu(II), Cd(II), and Pb(II) remain constant.

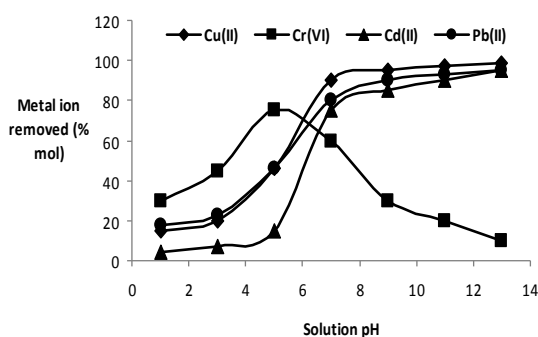
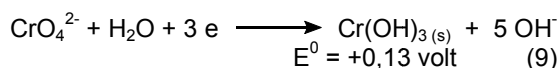


Fig. 3. The influence of the solution pH on the toxic metal ions removal by photocatalytic process

In the solution having pH 1- 5, all of Cu(II) exists as Cu²⁺ as seen in Fig. 4 of Copper Pourbaix diagram [16], that can be reduced into Cu(s). Based on this speciation, the degree of the removal is supposed to be same, but the degree is improved. The improvement may be induced by the speciation of TiO₂ surface. At pH 1-4, the surface of TiO₂ in the aqueous solution is found as a mixture of TiOH₂⁺ and TiOH, in which TiOH is more difficult to release electrons, than TiOH₂⁺. Increasing pH from 1 to 4, gives an increase in the fraction of TiOH, and TiOH is entirely found at pH 4-8 [5]. The increase of TiOH fraction can provide more electrons in the solution, explaining the rise of Cu(II) photo reduction degree. The sharp improvement of the removal degree as the pH increases from 3 to 5, is promoted by a lot of electrons provided by TiO₂ presence entirely as TiOH. The further sharp increasing in the Cu(II) removal degree when the pH was increased from 5 to 7, is caused by solid or precipitate of Cu(OH)₂ formation as seen in Fig. 4. The precipitate may cover the surface of TiO₂ solid, that is not found in the solution and undetected during the analysis by AAS. This explanation is supported by the fact that at pH 7-14, where Cu(II) ion is completely formed as precipitate of Cu(OH)₂, the removal of Cu(II) from the solution remains constant and reach maximum. It is clear

that the high removal at high pH is not caused by photoreduction, but due to the precipitation.

Species of Cr(VI) in the solution with pH 1-5, is found as HCrO_4^- which is in equilibrium with $\text{Cr}_2\text{O}_7^{2-}$ as illustrated by Fig.4 b and 4 c. The species of $\text{Cr}_2\text{O}_7^{2-}$ in solution with low pH can be easily reduced as indicated by high standard reduction potential as presented by reaction (5). The improvement of the removal degree as the increasing pH from 1 to 5, is resulted by increasing number of TiOH that can provide more electrons, as discussed above. Decreasing degree of Cr(VI) removal from the solution with pH higher than 5 can be caused by the formations of CrO_4^{2-} , TiO^- of the TiOH surface, and $\text{Cr}(\text{OH})_3$ precipitate. The species of CrO_4^{2-} is formed at pH higher than 6, as shown by Fig. 4b, that is lesser reducible than HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$, as indicated by the lower standard reduction potential as seen in reaction (9). As a consequence, the lower photoreduction is obtained.



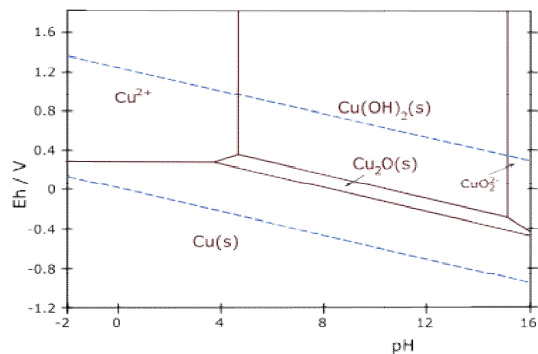
In addition, at pH higher than 5, Cr(III) ion resulted from Cr(VI) photoreduction is precipitated to form $\text{Cr}(\text{OH})_3$. The precipitate can inhibit the penetration of UV light into the solution, leading to the less effective photoreduction.

Based on the species of TiO_2 surface, at pH 5-8, TiOH is formed that can provide more electrons. This condition should give high photoreduction degree. It seems that in this condition, the photocatalyst does not play significant role. At pH higher than 8, TiO_2 surface is found as TiO^- giving less electrons, that can lead to the photoreduction decreased. In the such range pH, it seems that the species of TiO_2 surface also contributes on the decrease of the Cr(VI) removal degree.

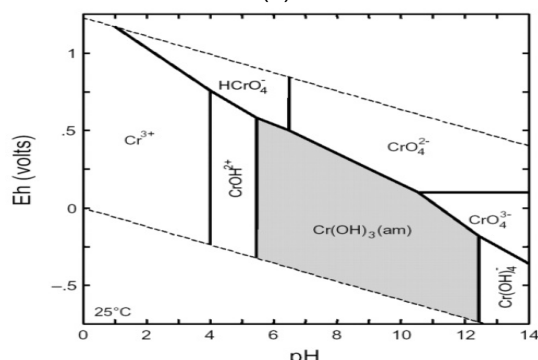
In the case of Cd(II), Cd^{2+} is completely formed in the solution with pH from 1-8, as illustrated by Fig. 5 b. The cation is easy to be adsorbed by the surface of TiO_2 . Based on this speciation,

the degree of the removal is supposed to be same. The change of the removal degree with the change of pH must be controlled by the species of TiO_2 surface. At low pH, the surface of TiO_2 existing as TiOH^+ that may inhibit the adsorption of Cd^{2+} and as TiOH that prefers to

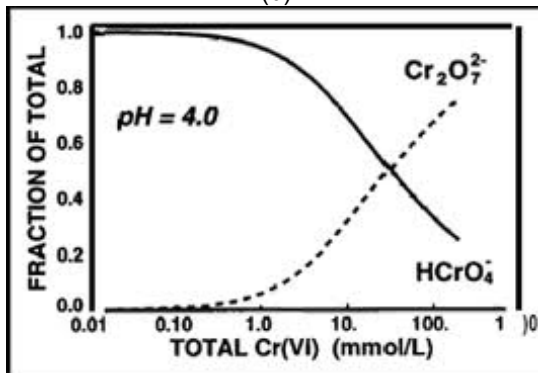
adsorb the cation. As the pH increases, the fraction of TiOH^+ decreases followed by the increase of TiOH fraction, promoting higher adsorption. At pH higher than 8, all of Cd (II) has precipitated as $\text{Cd}(\text{OH})_2$, and deposited on the surface of TiO_2 that cannot be measured in the solution. By AAS. It is obvious that the high degree of Cd (II) removal at high pH is not through adsorption, but by precipitation.



(a)

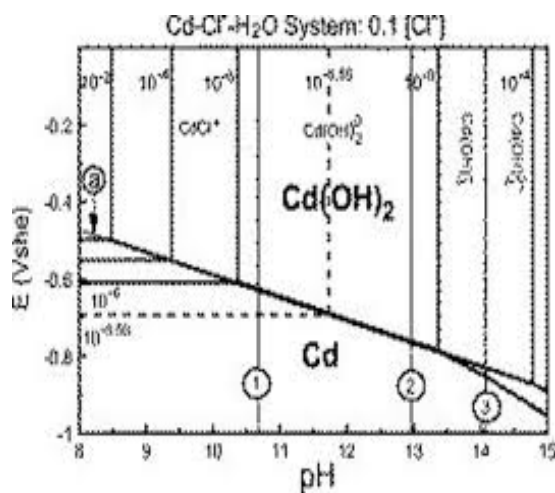


(b)

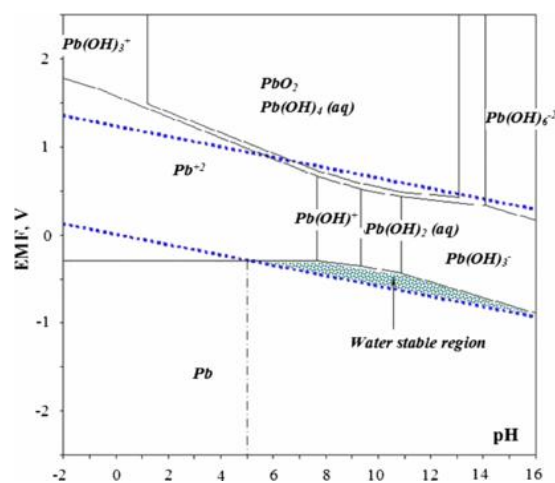


(c)

Fig. 4. The species of Cu and Cr in the solution with various pH



(a)



(b)

Fig. 5. The species of Cd and Pb in the solution with various pH

From Fig 5 b, it is seen that Pb(II) in the solution with pH 1-8, is fully found as Pb^{2+} that can be oxidized by OH radicals from water and photocatalyst [5] and the same degree of removal should be resulted. Thus, the enhance of the removal degree, as explained previously, is promoted by the increase of TiOH fraction in the solution. It takes the note that TiOH is easier to release electron as well as OH radical. In the solution with further increasing pH from 8 to 14, the species of Pb(II) is found as $Pb(OH)_2$ precipitate, that may be stacked on the surface of TiO_2 , that is undetected by AAS during analysis. It is obvious that the high degree of Pb(II) removal at high pH is promoted by precipitation as happen in $Cu(OH)_2$ and $Cd(OH)_2$.

3.3 The Influence of Other Metal Ions on Cu(II) Photocatalytic Reduction

In wastewater, Cu(II) ions can be along together with some heavy metal ions such as Cr(VI), Cd(II), and Pb(II). Accordingly, the influence of Cr(VI), Cd(II), and Pb(II) ions on the Cu(II) removal under UV light irradiation was observed. The reaction took place in the solution with pH 4, in which the species of Cu(II), Cr(VI), Cd(II), and Pb(II) are formed as Cu^{2+} , $HCrO_4^-$ and $Cr_2O_7^{2-}$, Cd^{2+} and Pb^{2+} , respectively. The result is displayed as Fig. 6, illustrating that the presence of both $HCrO_4^-$ and $Cr_2O_7^{2-}$ as well as Cd^{2+} ions leads to the degree of Cu^{2+} removal decreased. In contrast, the enhancement of Cu^{2+} photoreduction degree is observed when Pb^{2+} was added in the solution. The species of $HCrO_4^-$ and $Cr_2O_7^{2-}$ can make the Cu^{2+} photoreduction decreased because of the competition in the photoreduction. Meanwhile decreasing Cu^{2+} photoreduction caused by Cd^{2+} is induced by competition in the adsorption. The effect of decreasing Cu^{2+} photoreduction shown by $HCrO_4^-$ and $Cr_2O_7^{2-}$ is higher than that of by Cd^{2+} . As presented above that $HCrO_4^-$ and $Cr_2O_7^{2-}$ is faster to be reduced than Cu^{2+} giving strong competition, while the affinity of Cu^{2+} and Cd^{2+} in the adsorption on the surface of TiO_2 is not significantly different explaining the low effect of Cd^{2+} in decreasing Cu^{2+} photoreduction.

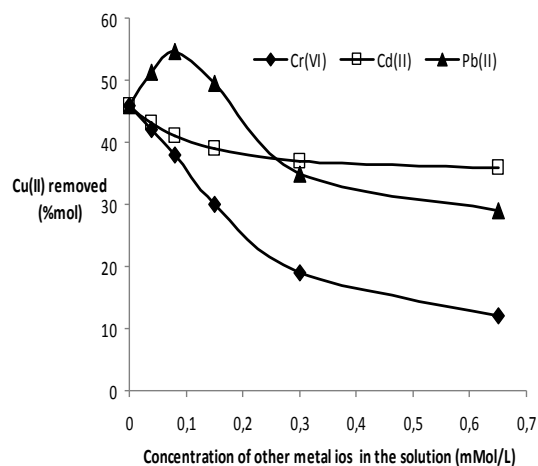


Fig. 6. The influence of the presence of other toxic metal ions on the Cu(II) photoreduction

It is also observed that the presence of Pb^{2+} shows interesting effect on Cu^{2+} photoreduction. Increasing Pb^{2+} concentration has enhanced the degree of Cu^{2+} removal, but the degree goes down when the concentration of Pb^{2+} ion is

further increased. In the photocatalytic reaction, Pb^{2+} ion is oxidized simultaneously with the reduction of Cu^{2+} , promoting in the synergic effect. Such effect is implied by the increase of Cu^{2+} photoreduction. On the other hand the oxidation of Pb^{2+} forming PbO_2 solid can inhibit the light penetration, that can reduce the production of OH radical for oxidation. The higher $Pb(II)$ concentration can result in more PbO_2 giving more inhibition. It is clear that in the low $Pb(II)$ concentration the synergic effect is prominent, but in the higher $Pb(II)$ concentration, the inhibition effect plays stronger role.

4. CONCLUSION

It is concluded that the removal of $Cd(II)$, $Cr(VI)$ as well $Cu(II)$ and $Pb(II)$ ions from the water has been successfully carried out by respective adsorption, photoreduction and photooxidation. The removal of the studied metal ions is controlled by pH solution, and the most effective removal is achieved at pH 5. The presence of $Cr(VI)$ and $Cd(II)$ with all range given concentrations lead to a decrease in the removal of $Cu(II)$ by competition in photoreduction and adsorption respectively, meanwhile synergic effect, that enhances the $Cu(II)$ photoreduction, is shown by $Pb(II)$ ion in the low concentration but contrary effect is observed for high $Pb(II)$ concentration. However, the mutual effect of $Cd(II)$, $Cu(II)$, and $Pb(II)$ on the photoreduction of $Cr(VI)$ has not been evaluated, so it is suggested to be further assessed.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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