



A Study on the Photocatalytic Reduction of Some Metal Ions in Aqueous Solution Using UV- Titanium Dioxide System

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Authors' contributions

This work was carried out in collaboration among all authors. Authors IOE and MH designed the study. Author IOE wrote the protocol and the first draft of the manuscript. Authors IOE, MH and JOEO managed the analyses of the study. Author JOEO prove read the manuscript. Authors IOE and JOEO managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The photocatalytic reduction of Cu (II), Pb (II), Cd (II) and Cr (VI) ions in aqueous solution has been investigated. The photocatalyst utilized was nano titanium dioxide, composed of 80% anatase and 20% rutile; the UV light source was a 15 W UV bulb with a wavelength of 254 nm. The results obtained indicated a reduction efficiency order as follows; $\text{Cr}^{6+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$. It was observed that these results correlate with the respective reduction potentials of the metal ions. The effect of pH on the photocatalytic reduction of the metal ions was also carried out and results obtained indicated that with the exception of Cr (VI) ions, higher percentage removal of metal ions from their aqueous solution was recorded at alkaline pH than at acidic pH. This was attributed to an extensive formation of precipitate by the metal ions at alkaline pH. Kinetic studies revealed that the removal of metal ions from their solutions largely followed the pseudo- first-order kinetics. Therefore, the results of this study will be useful in metal ion removal from industrial waste water using photocatalytic process.

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1. INTRODUCTION

The presence of metal ions in waste effluents poses a serious health problem to humans since most metal ions are toxic to plants and animals. Thus, efforts at the removal of metal ions from waste water have attracted significant interest from environmentalists globally. Some conventional methods employed include, adsorption on biosorbents, membrane filtration, sedimentation, electrodialysis, ion exchange processes etc. However, this study is focused on the photocatalytic method of removing metal ions from their aqueous solutions. The main advantages of this process over other water treatment methods include its suitability over a wide range of pollutants, complete chemical transformation / destruction of pollutants, economic viability and no generation of waste during the process.

The fact that metals are elements that do not degrade in the environment means that they are highly persistent, resulting in a greater potential for exposure to organisms than other less persistent, toxic chemicals [1]. Therefore, there is need for an efficient treatment method of heavy metal contaminated waste water.

Fox and Dulay, [2] found that irradiated semiconductor particles could catalyze a lot of interesting and useful reduction-oxidation reactions of organic and inorganic compounds. Some semiconductors, also known as photocatalyst, when illuminated with light of

suitable energy generate holes and electrons in their valence and conduction band respectively (see Fig. 1). The holes and electrons are charge carriers, capable of oxidizing and reducing pollutant species in solution [3]. The reduction of metal ions takes place at the conduction band, where the metal ions are reduced to a lower or zerovalent oxidation state as shown in equation 1.



2. METHODS

All reagents were of analytical grade and were used as received. The TiO₂ was nano sized and supplied by US Nano Inc., USA. The titanium dioxide consisted of 80% anatase and 20% rutile, 20 nm particle size with a solid surface area (SSA) of 20 – 45 m²/g. Fig. 2 shows a schematic diagram of the photoreactor which was employed in this study. The photoreactor is a rectangular box with outer dimension of 67 cm × 30 cm × 33 cm. The interior of the box was completely painted black and sealed to screen out reflected light. A 15W UV bulb (T8 15 W UVC) with wavelength range of 254 nm was fastened at the top of the interior area of the photoreactor box. The UV bulb is a germicidal lamp made up of soda lime glass and contains mercury at low pressure. Two electronic magnetic stirrers were placed inside the photoreactor box to facilitate the continuous stirring of the sample during photoreduction experiment.

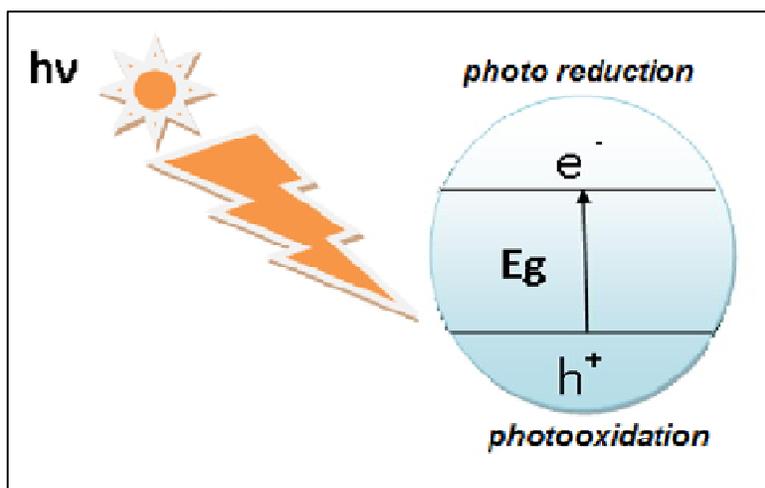


Fig. 1. Generation of holes and electrons in a photocatalyst under illumination

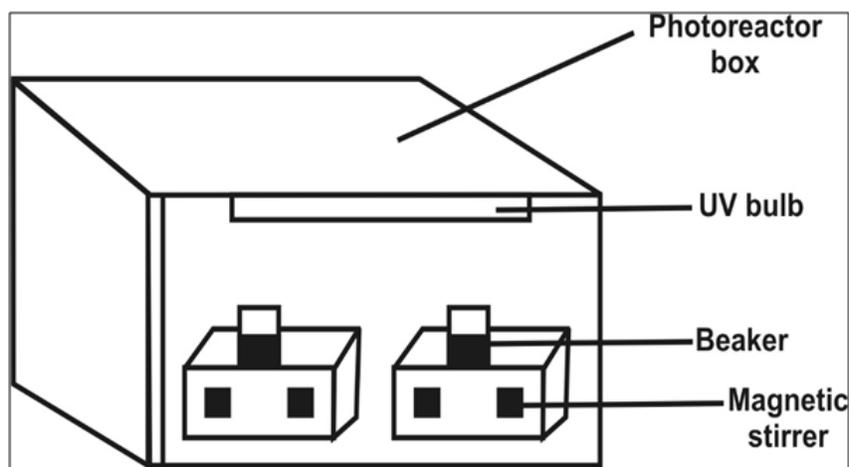


Fig. 2. Schematic diagram of the photoreactor design

The metal salts used in this study were $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, CdCl_2 and $\text{K}_2\text{Cr}_2\text{O}_7$ for the photocatalytic reduction investigations of Cu (II), Pb (II), Cd (II) and Cr (VI) ions respectively. 50 ml of 200 ppm of the metal ions solutions were measured into a 100 ml beaker and 0.2 g of TiO_2 was next added. The solution was stirred with a magnetic stirrer continuously while being irradiated with a 15 W UV light in the photoreactor. Photoreduction was investigated at various reaction times of 0, 30, 60 and 90 minutes respectively and at a pH of 5. At the end of each experiment, the metal salt solution was centrifuged and then analysed using the AAS, with the exception of $\text{K}_2\text{Cr}_2\text{O}_7$ solution which was analysed with

UV/Vis. The determination of Cr (VI) reduction was carried out using the EPA METHOD 7196A (Colometric). In this method, the dissolved hexavalent chromium reacts with 1-5-diphenylcarbazide ($\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$) in an acidic solution producing a violet colored compound, and the absorbance measured at 540 nm is proportional to Cr (VI) concentration.

The effects of pH on the photoreduction of Cu (II), Cd (II), Pb (II) and Cr (VI) ions were investigated by varying the pH (3, 5, 7, 9 and 11), while the initial concentration of the metal solution, catalyst load and reaction time were fixed at 200 ppm, 4 g/l and 60 minutes respectively.

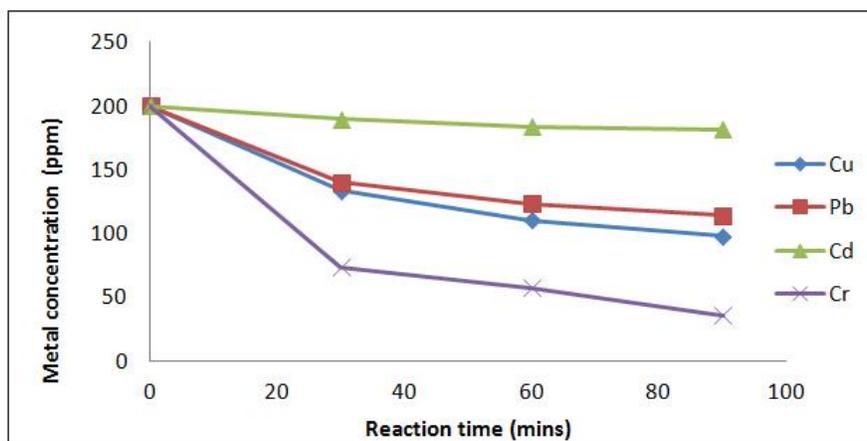


Fig. 3. Metal ion concentration (ppm) against reaction time (mins) (Reaction conditions: initial concentration 200 ppm, catalyst dose 4g/l, pH 5, 15 W UV light)

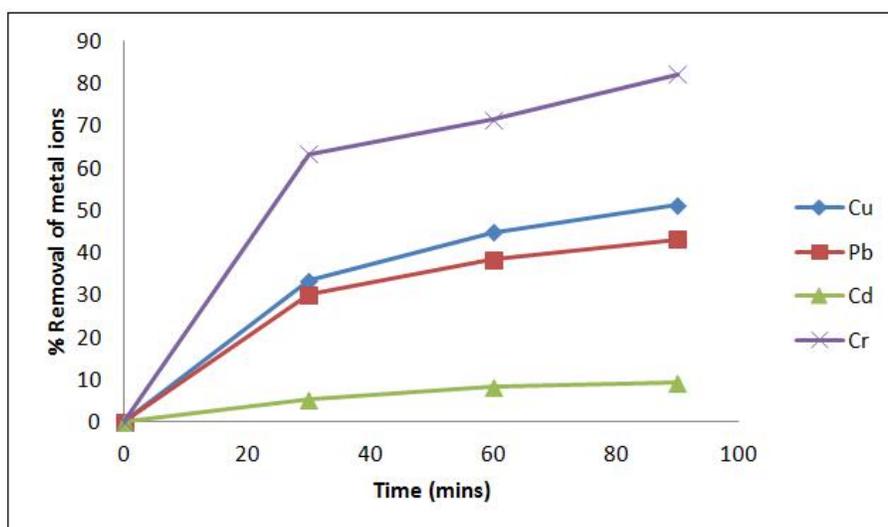
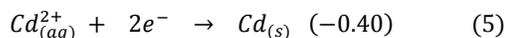
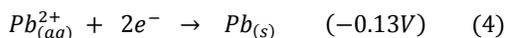
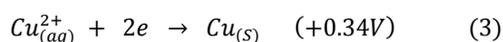
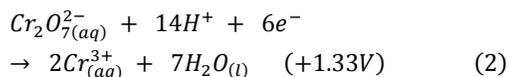


Fig. 4. Effect of photoreduction time on the % removal of metal ions from their solution (Reaction conditions: initial metal ion conc. 200 ppm, cat. dose 4 g/l, pH 5, 15W UV light)

3. RESULTS AND DISCUSSION

3.1 Photoreduction of Metal ions in Solution

The reduction of the metal ions depends on their reduction potential as shown in the equations below;



Elements with higher reduction potentials are more easily reduced than the ones with lower or negative reduction potential [4]. In this research, the photoreduction of Cd^{2+} , Cu^{2+} , Pb^{2+} and Cr^{6+} ions were investigated using the TiO_2/UV system. Photoreduction efficiencies of these metal ions are as shown in Fig. 4. In general, it was observed that Cr^{6+} recorded the highest photoreduction efficiency of 82.1% after 90 minutes of reaction time at pH 5. In comparison, reduction of the other ions at similar reaction conditions is as follows: Cd (59.3%), Pb (43.1%) and Cu (51.21%). It is interesting to observe that these results correlate with the respective

reduction potentials of these metals which follow the trend: $\text{Cr}^{6+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$ (as seen in equations 2-5).

3.2 Effect of pH on Photoreduction of Metals

The effect of pH on the reduction of metal ions was also investigated and this is shown in Fig. 5. From pH 3 - 11, the reduction efficiency range are as follows: Cd (2.45% - 85.342%), Cu (15.2% - 90.51%), Pb (16.2% - 85.05%) and Cr (34.51% - 23.2%). With the exception Cr (VI), it was observed that the reduction of the metal ions increased gradually from acidic medium to basic medium, that is, the highest removal of metal was recorded at basic pH. This can be attributed to two main factors namely; the precipitation of the metal ions at basic medium and the structure of the photocatalyst at different pH medium. At pH 1 - 4, TiO_2 surface is a mixture of TiOH_2^+ and TiOH [5]. Increasing the pH from 1 - 4 gives an increase in the fraction of TiOH ; TiOH is entirely found at pH 5 - 8 and from pH 8 -14, the TiO_2 surface is predominantly TiO^- [5]. At alkaline medium, metal ions precipitate out of the solution to form their respective hydroxides and oxides. Therefore, since Pb and Cd ions have negative reduction potentials as shown in equations 4 and 5, their increased removal from their aqueous solution in basic pH cannot be due to photoreduction but may be attributed to their increased adsorption on negatively charged TiO_2 surface (since they are cations). Their enhanced removal, can also be due to their precipitation

from their solution at basic medium, for instance, Cu^{2+} ions precipitate out of solution to form $\text{Cu}(\text{OH})_2$ and Cd^{2+} ions precipitate to $\text{Cd}(\text{OH})_2$. As a result, the metals are not detected when the resulting solution is analysed by AAS instrument. Since Pb^{2+} ions can be oxidized to Pb (IV) oxide, the removal of some Pb ions from its aqueous solution during the photocatalytic process may be due to the photo-oxidation of Pb^{2+} to PbO_2 . On the other hand, the photoreduction of Cr^{6+} ions is inhibited at higher pH because Cr^{6+} ions exist as CrO_4^{2-} ions in solution and therefore are not easily adsorbed on the negatively charged TiO_2 surface at basic pH. This result corresponds with the finding of [6], who stated that during the photocatalytic removal of Cr (VI), the reduction rate of dichromate ions gradually decreased because the increase in pH value reduced the adsorption of dichromate ions on the surface of the photocatalyst; similarly, at high pH value, $\text{Cr}(\text{OH})_3$ covered the surface active position of TiO_2 so that the trivalent chromium

deposited on TiO_2 depressed the photocatalytic activity.

3.3 Kinetics of Reduction of Metal Ions

The kinetics of the reduction of metal ions in the TiO_2/UV system was also found to follow the pseudo-first-order kinetics. The R^2 values ranged from 0.889 for Pb (II) ions reduction kinetics plot to 0.926 in Cu (II) and Cr (VI) ions photoreduction kinetic plot, as shown in Table 1. The trend of their k_1 values are given as Cr (0.018 mins^{-1}) > Cu (0.007 mins^{-1}) > Pb (0.006 mins^{-1}) > Cd (0.001 mins^{-1}). This shows a decreasing rate of metal ion reduction from Cr (VI) ions, with the highest rate of reduction to Cd (II) ions, as a result of the least rate of reduction. Interestingly, this trend corresponds with their reduction potentials given as:

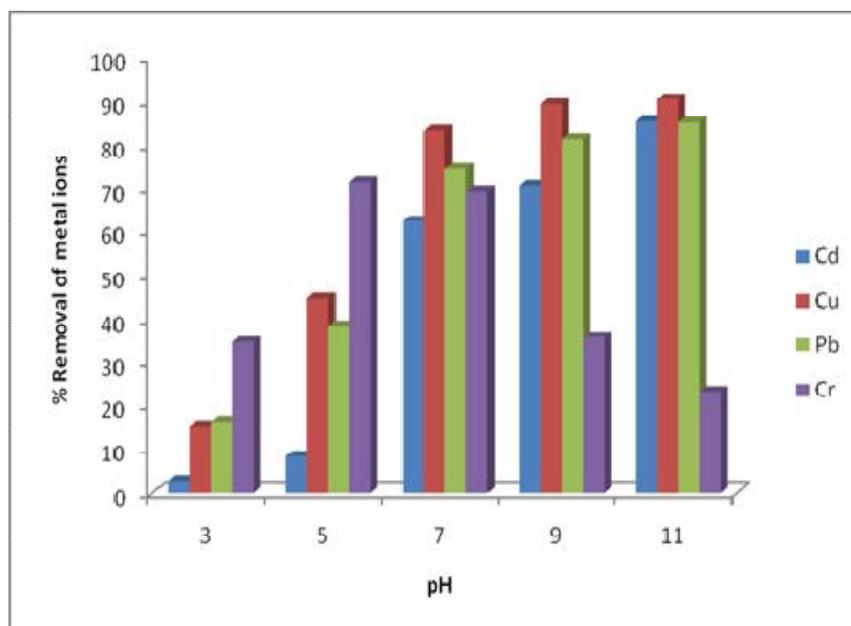
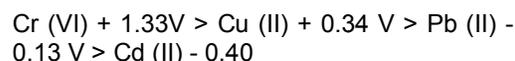


Fig. 5. Effect of pH on the %Removal of metal ions from their solution (Reaction conditions: initial metal ion conc. 200 ppm, reaction time 60 mins, cat. dose 4 g/l)

Table 1. Pseudo first order parameters for heavy metals photoreduction

| Sample | K_1 (mins^{-1}) | R^2 values |
|--------|------------------------------|--------------|
| Cu | 0.007 | 0.926 |
| Pb | 0.006 | 0.889 |
| Cd | 0.001 | 0.922 |
| Cr | 0.018 | 0.926 |

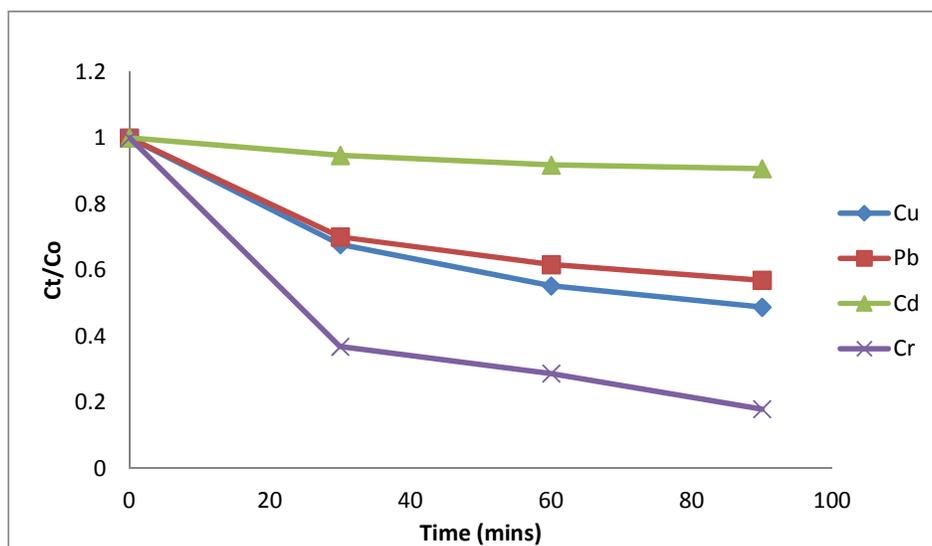


Fig. 6. Photoreduction kinetics for the metal ions in their solution (Reaction conditions: Initial metal ion conc. 200 ppm, cat. dose 4 g/l, pH 5, 15 W UV light, nano TiO₂ PC)

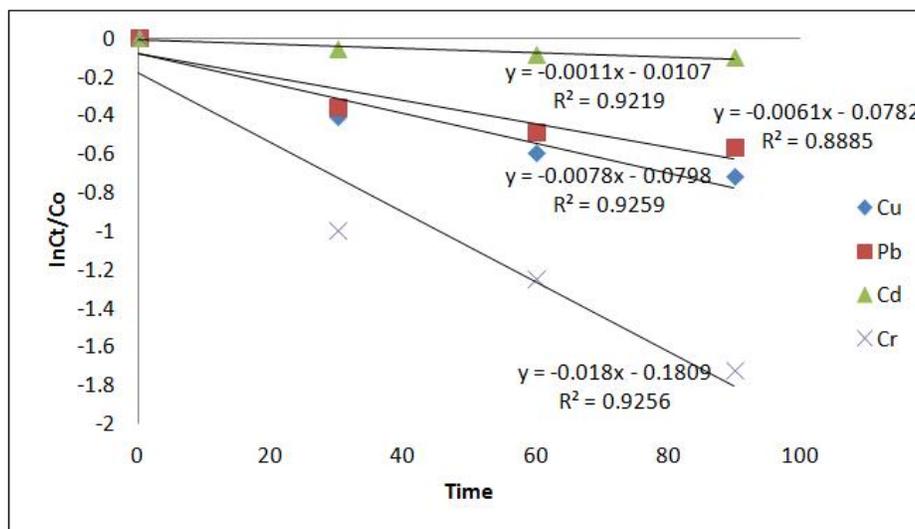


Fig. 7. Pseudo-first-order kinetics plot for the photoreduction of metal ions in their solution (Reaction conditions: initial metal ion conc. 200 ppm, cat. dose 4 g/l, pH 5, 15 W UV light, nano TiO₂ PC)

Therefore, the rate of photoreduction of metal ions is dependent only on the concentration of the metal ions in solution. However, it was stated earlier that the removal of the metal ions, with negative reduction potential, from their solutions is not due to the reduction of their ions in solution but as a result of adsorption on the surface of the photocatalyst, precipitation of the ions to form hydroxides and even oxidation of the cations to oxides, as in the case of Pb.

4. CONCLUSION

The removal of the metal ions from their aqueous solutions has been successfully achieved. Cu (II) and Cr (VI) ions gave the highest reduction rate while Cd (II) ions recorded the least reduction rate. A correlation was made between the photocatalytic reduction rate of the metal ions and their respective reduction potentials. Furthermore, it was found that the removal of the

metal ions was highest at pH 11 (with exception of Cr⁶⁺ ions) while the least metal ion removal efficiency was pH 3; this was attributed to the formation of precipitates by the metal ions at alkaline pH. This study also revealed that the kinetics of the metal ion reduction largely followed the pseudo-first-order kinetics.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Beckett WS, Nordberg GF, Clarkson TW. Routes of exposure, dose, and metabolism of metals. In Handbook on the Toxicology of Metals (3rd Ed). Academic Press, MA. 2007;39–64.
2. Fox M, Dulay M. Heterogenous photocatalysis. Chemical Reviews. 1993;93:341–357.
3. Barakat MA. New trends in removing heavy metals from industrial wastewater. Arabian Journal of Chemistry. 2011;4:361–377.
4. Williams PL, James RC, Roberts SM. Principles of toxicology: Environmental and industrial applications (2nd Ed.). John Wiley and Sons, N.Y. 2000;325–374.
5. Wahyuni ET, Aprilita NH, Hatimah H, Wulandari AM, Mudasir M. Removal of toxic metals in water by photocatalytic method. American Chemical Society Journal. 2015;5(2):194–201.
6. Ma CM, Shen YS, Lin PO. Photoreduction of Cr(VI) ions in aqueous solutions by UV/TiO₂ photocatalytic process. International Journal of Photoenergy; 2012. ID: 381971. DOI: 10.1155/2012/38197

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