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3 **A STUDY ON THE PHOTOCATALYTIC REDUCTION OF SOME METAL IONS IN**  
4 **AQUEOUS SOLUTION USING UV- TITANIUM DIOXIDE SYSTEM**

5  
6 **ABSTRACT**

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

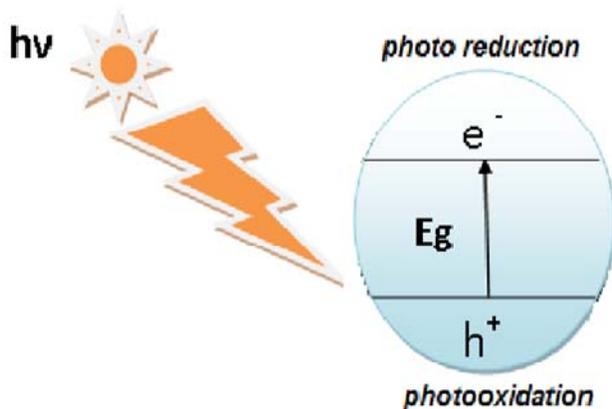
19 *Keywords: Photocatalysts, Photocatalytic reduction, Titanium Dioxide, Kinetic study*

20 **INTRODUCTION**

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

30 The fact that metals are elements that do not degrade in the environment means that they are  
31 highly persistent, resulting in a greater potential for exposure to organisms than other less  
32 persistent, toxic chemicals (Beckett *et al.*, 2007). Therefore, there is need for an efficient  
33 treatment method of heavy metal contaminated waste water.

34 Fox and Dulay, 1993 found that irradiated semiconductor particles could catalyze a lot of  
35 interesting and useful reduction-oxidation reactions of organic and inorganic compounds. Some  
36 semiconductors, also known as photocatalyst, when illuminated with light of suitable energy  
37 generate holes and electrons in their valence and conduction band respectively (see fig. 1). The  
38 holes and electrons are charge carriers, capable of oxidizing and reducing pollutant species in  
39 solution (Barakat, 2014). The reduction of metal ions takes place at the conduction band, where  
40 the metal ions are reduced to a lower or zerovalent oxidation state as shown in equation 1

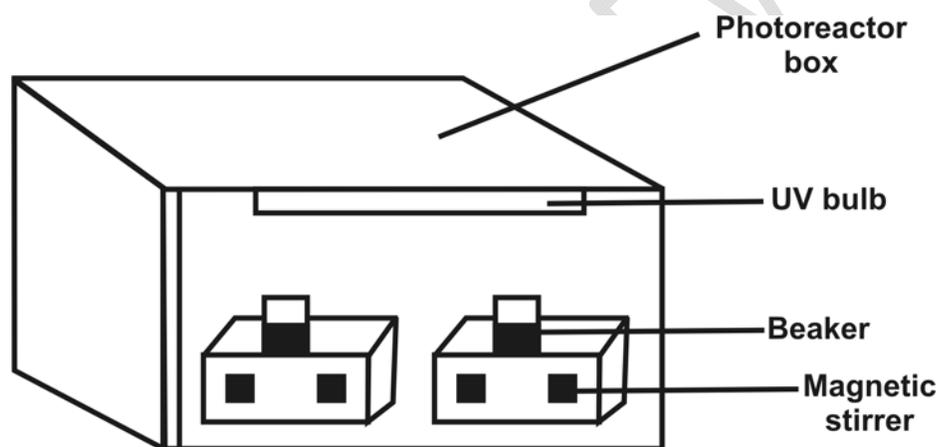


41 **Fig. 1 Generation of holes and electrons in a photocatalyst under illumination**

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44 **METHODS**

45 All reagents were of analytical grade and were used as received. The TiO<sub>2</sub> was nano sized and  
46 supplied by US Nano Inc., USA. The titanium dioxide consisted of 80% anatase and 20% rutile,

47 20 nm particle size with a solid surface area (SSA) of 20 – 45 m<sup>2</sup>/g. Fig. 2 shows a schematic  
48 diagram of the photoreactor which was employed in this study. The photoreactor is a rectangular  
49 box with outer dimension of 67 cm × 30 cm × 33 cm. The interior of the box was completely  
50 painted black and sealed to screen out reflected light. A 15W UV bulb (T8 15 W UVC) with  
51 wavelength range of 254 nm was fastened at the top of the interior area of the photoreactor box.  
52 The UV bulb is a germicidal lamp made up of soda lime glass and contains mercury at low  
53 pressure. Two electronic magnetic stirrers were placed inside the photoreactor box to facilitate  
54 the continuous stirring of the sample during photoreduction experiment.



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56 **Fig. 2 Schematic diagram of the photoreactor design**

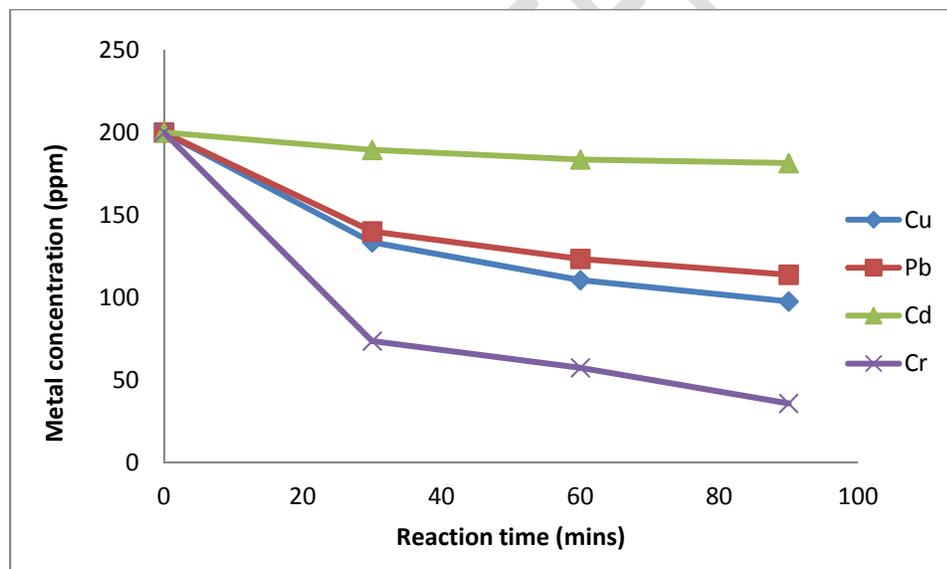
57 The metal salts used in this study were Cu (NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Pb (NO<sub>3</sub>)<sub>2</sub>, CdCl<sub>2</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> for  
58 the photocatalytic reduction investigations of Cu (II), Pb (II), Cd (II) and Cr (VI) ions  
59 respectively. 50 ml of 200 ppm of the metal ions solutions were measured into a 100 ml beaker  
60 and 0.2 g of TiO<sub>2</sub> was next added. The solution was stirred with a magnetic stirrer continuously  
61 while being irradiated with a 15 W UV light in the photoreactor. Photoreduction was  
62 investigated at various reaction times of 0, 30, 60 and 90 minutes respectively and at a pH of 5.  
63 At the end of each experiment, the metal salt solution was centrifuged and then analysed using

64 the AAS, with the exception of  $K_2Cr_2O_7$  solution which was analysed with UV/Vis. The  
65 determination of Cr (VI) reduction was carried out using the EPA METHOD 7196A  
66 (Colometric). In this method, the dissolved hexavalent chromium reacts with 1-5-  
67 diphenylcarbazide ( $C_{13}H_{14}N_4O$ ) in an acidic solution producing a violet colored compound, and  
68 the absorbance measured at 540 nm is proportional to Cr (VI) concentration.

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

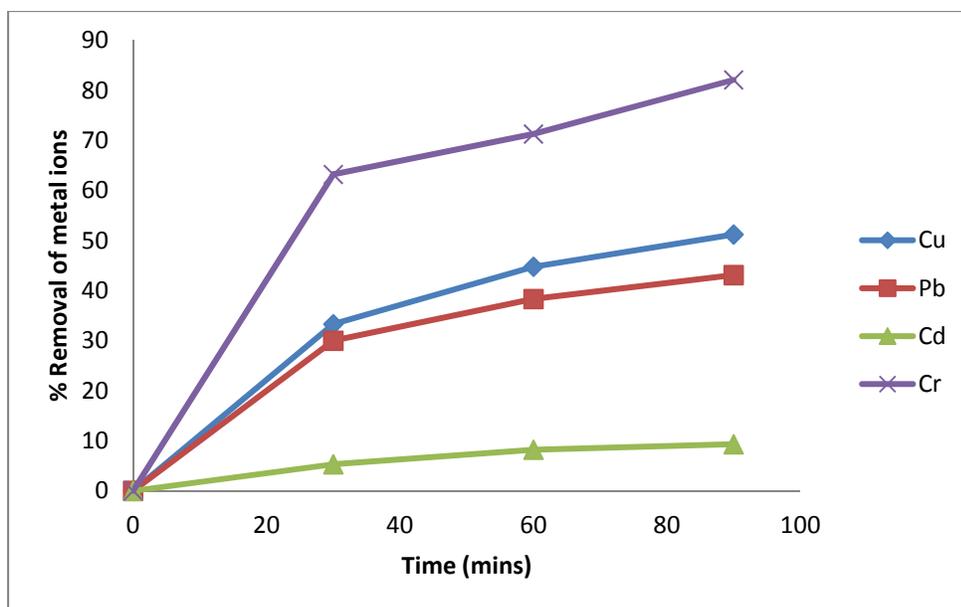
## 73 RESULTS AND DISCUSSION

### 74 Photoreduction of Metal ions in solution



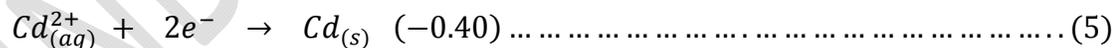
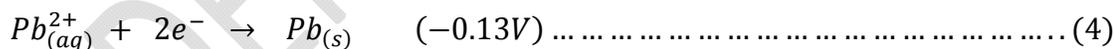
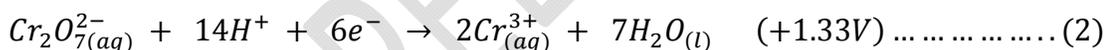
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76 **Fig. 3 Metal ion concentration (ppm) against reaction time (mins) (Reaction conditions:**  
77 **initial concentration 200 ppm, catalyst dose 4g/l, pH 5, 15 W UV light)**

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79  
 80 **Fig. 4 Effect of photoreduction time on the % removal of metal ions from their solution**  
 81 **(Reaction conditions: initial metal ion conc. 200 ppm, cat. dose 4 g/l, pH 5, 15W UV light)**

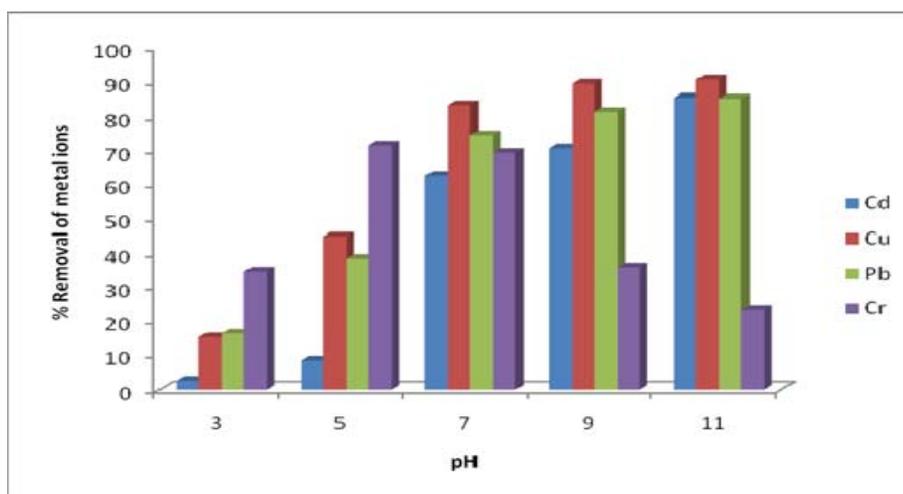
82 The reduction of the metal ions depends on their reduction potential as shown in the equations  
 83 below;



84 Elements with higher reduction potentials are more easily reduced than the ones with lower or  
 85 negative reduction potential (Williams *et al.*, 2000). In this research, the photoreduction of  $Cd^{2+}$ ,  
 86  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Cr^{6+}$  ions were investigated using the  $TiO_2/UV$  system. Photoreduction  
 87 efficiencies of these metal ions are as shown in fig. 4. In general, it was observed that  $Cr^{6+}$   
 88 recorded the highest photoreduction efficiency of 82.1% after 90 minutes of reaction time at pH

89 5. In comparison, reduction of the other ions at similar reaction conditions is as follows: Cd  
90 (59.3%), Pb (43.1%) and Cu (51.21%). It is interesting to observe that these results correlate with  
91 the respective reduction potentials of these metals which follow the trend:  $\text{Cr}^{6+} > \text{Cu}^{2+} > \text{Pb}^{2+} >$   
92  $\text{Cd}^{2+}$  (as seen in equations 2-5)

### 93 Effect of pH on Photoreduction of Metals



94  
95 **Fig. 5 Effect of pH on the %Removal of metal ions from their solution (Reaction conditions: initial**  
96 **metal ion conc. 200 ppm, reaction time 60 mins, cat. dose 4g/l)**  
97

98 The effect of pH on the reduction of metal ions was also investigated and this is shown in fig.5.  
99 From pH 3 - 11, the reduction efficiency range are as follows: Cd (2.45% - 85.342%), Cu (15.2%  
100 - 90.51%), Pb (16.2% - 85.05%) and Cr (34.51% - 23.2%). With the exception Cr (VI), it was  
101 observed that the reduction of the metal ions increased gradually from acidic medium to basic  
102 medium, that is, the highest removal of metal was recorded at basic pH. This can be attributed to  
103 two main factors namely; the precipitation of the metal ions at basic medium and the structure of  
104 the photocatalyst at different pH medium. Wahyuni *et al.*, 2015, indicated that at pH 1 - 4,  $\text{TiO}_2$   
105 surface is a mixture of  $\text{TiOH}_2^+$  and  $\text{TiOH}$ . Increasing the pH from 1 - 4 gives an increase in the  
106 fraction of  $\text{TiOH}$ ;  $\text{TiOH}$  is entirely found at pH 5 - 8 and from pH 8 -14, the  $\text{TiO}_2$  surface is

107 predominantly  $\text{TiO}^-$ . At alkaline medium, metal ions precipitate out of the solution to form their  
108 respective hydroxides and oxides. Therefore, since Pb and Cd ions have negative reduction  
109 potentials as shown in equations (4) and (5), their increased removal from their aqueous solution  
110 in basic pH cannot be due to photoreduction but may be attributed to their increased adsorption  
111 on negatively charged  $\text{TiO}_2$  surface (since they are cations). Their enhanced removal, can also be  
112 due to their precipitation from their solution at basic medium, for instance,  $\text{Cu}^{2+}$  ions precipitate  
113 out of solution to form  $\text{Cu}(\text{OH})_2$  and  $\text{Cd}^{2+}$  ions precipitate to  $\text{Cd}(\text{OH})_2$ . As a result, the metals are  
114 not detected when the resulting solution is analysed by AAS instrument. Since  $\text{Pb}^{2+}$  ions can be  
115 oxidized to Pb (IV) oxide, the removal of some Pb ions from its aqueous solution during the  
116 photocatalytic process may be due to the photo-oxidation of  $\text{Pb}^{2+}$  to  $\text{PbO}_2$ . On the other hand, the  
117 photoreduction of  $\text{Cr}^{6+}$  ions is inhibited at higher pH because  $\text{Cr}^{6+}$  ions exist as  $\text{CrO}_4^{2-}$  ions in  
118 solution and therefore are not easily adsorbed on the negatively charged  $\text{TiO}_2$  surface at basic  
119 pH. This result corresponds with the finding of Ma *et al.*, 2012 who stated that during the  
120 photocatalytic removal of Cr (VI), the reduction rate of dichromate ions gradually decreased  
121 because the increase in pH value reduced the adsorption of dichromate ions on the surface of the  
122 photocatalyst; similarly, at high pH value,  $\text{Cr}(\text{OH})_3$  covered the surface active position of  $\text{TiO}_2$   
123 so that the trivalent chromium deposited on  $\text{TiO}_2$  depressed the photocatalytic activity.

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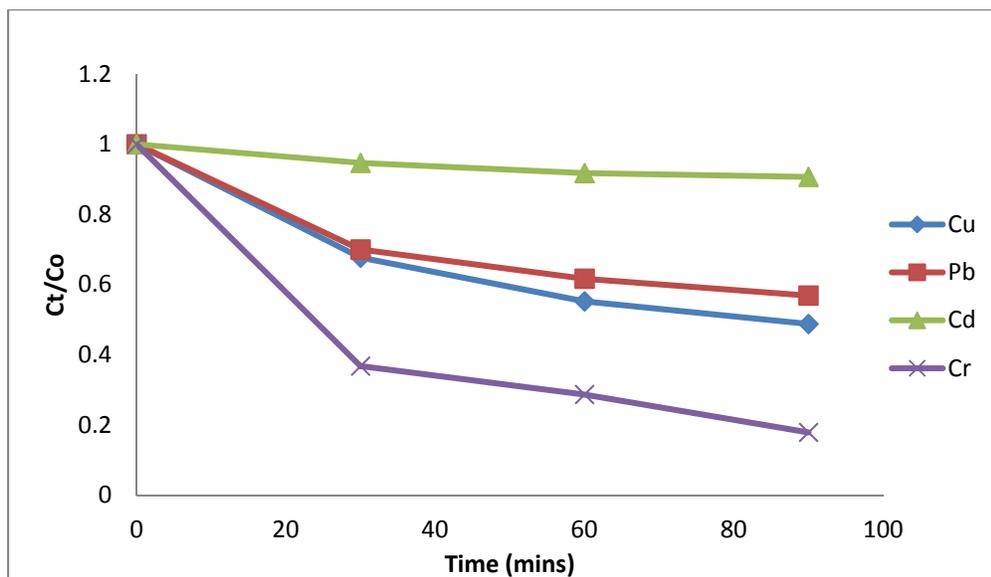
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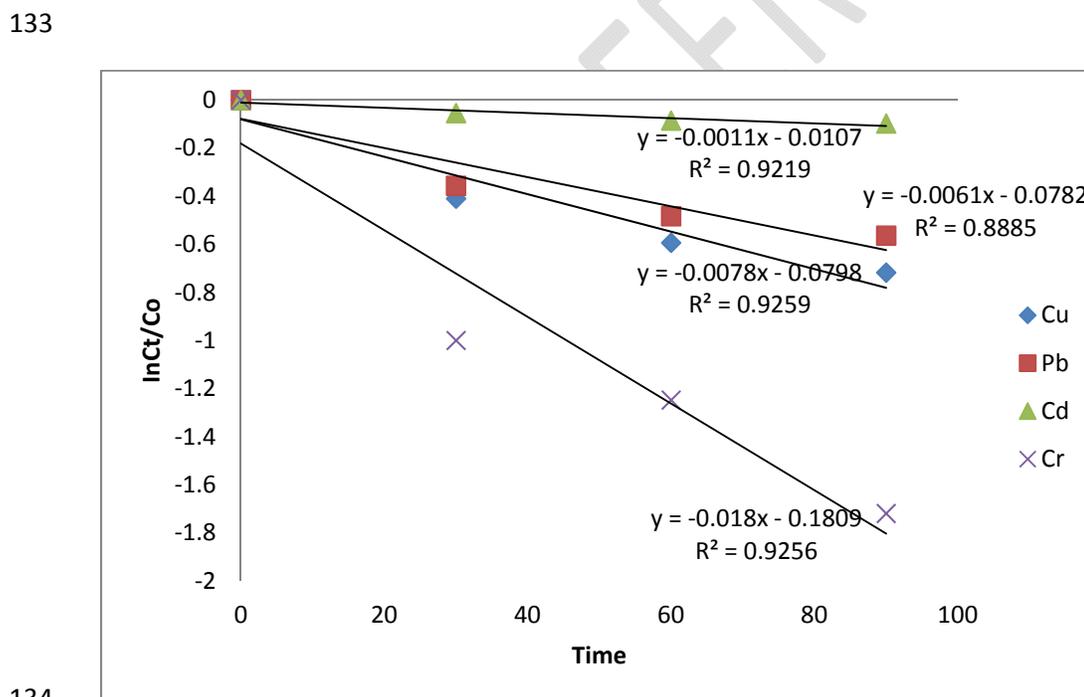
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129 **Kinetics of Reduction of Metal ions**



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131 **Fig. 6 Photoreduction kinetics for the metal ions in their solution (Reaction conditions:**  
132 **initial metal ion conc. 200ppm, cat. dose 4g/l, pH 5, 15 W UV light, nano TiO<sub>2</sub> PC)**



134  
135 **Fig. 7 Pseudo-first-order kinetics plot for the photoreduction of metal ions in their solution**  
136 **(Reaction conditions: initial metal ion conc. 200ppm, cat. dose 4g/l, pH 5, 15 W UV light,**  
137 **nano TiO<sub>2</sub> PC)**

138 **Table 1 Pseudo first order parameters for heavy metals photoreduction**

Sample	$K_1$ (mins <sup>-1</sup> )	$R^2$ values
Cu	0.007	0.926
Pb	0.006	0.889
Cd	0.001	0.922
Cr	0.018	0.926

139  
140 The kinetics of the reduction of metal ions in the TiO<sub>2</sub>/UV system was also found to follow the  
141 pseudo-first-order kinetics. The  $R^2$  values ranged from 0.889 for Pb (II) ions reduction kinetics  
142 plot to 0.926 in Cu (II) and Cr (VI) ions photoreduction kinetic plot, as shown in table 1. The  
143 trend of their  $k_1$  values are given as Cr (0.018 mins<sup>-1</sup>) > Cu (0.007 mins<sup>-1</sup>) > Pb (0.006 mins<sup>-1</sup>) >  
144 Cd (0.001 mins<sup>-1</sup>). This shows a decreasing rate of metal ion reduction from Cr (VI) ions, with  
145 the highest rate of reduction to Cd (II) ions, as a result of the least rate of reduction. Interestingly,  
146 this trend corresponds with their reduction potentials given as: Cr (VI) + **1.33V** > Cu (II) + **0.34**  
147 **V** > Pb (II) - **0.13 V** > Cd (II) - **0.40**

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

153

## 154 **CONCLUSION**

155 The removal of the metal ions from their aqueous solutions has been successfully achieved. Cu  
156 (II) and Cr (VI) ions gave the highest reduction rate while Cd (II) ions recorded the least

157 reduction rate. A correlation was made between the photocatalytic reduction rate of the metal  
158 ions and their respective reduction potentials. Furthermore, it was found that the removal of the  
159 metal ions was highest at pH 11 (with exception of Cr<sup>6+</sup> ions) while the least metal ion removal  
160 efficiency was pH 3; this was attributed to the formation of precipitates by the metal ions at  
161 alkaline pH. This study also revealed that the kinetics of the metal ion reduction largely followed  
162 the pseudo-first-order kinetics.

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