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Removal of Cr (VI) and Cu (II) Ions from Synthetic Wastewater by Solar Photocatalytic Reactor

Abstract- *Heavy metal ions in wastewater have promoted increasing concern on environmental and health risks. The present work was devoted to investigate the feasibility of utilizing solar light to degrade Cr (VI) and Cu (II) ions in synthetic wastewater. The effect of the key process parameters on the quality of product was studied by varying the pH (3, 5, 7, 9, and 11), H_2O_2 (50, 100, 200, and 300 mg/L) and TiO_2 loading (0.9, 1.3, and 1.7 g/L). Experimental results revealed that after 120 min of solar illumination the highest reduction of Cr (VI) ions was 97.0% obtained under (pH = 3, catalyst loading = 1.3 g TiO_2/L, and H_2O_2 =100 mg/L) and for Cu (II) ions the highest reduction was 97.7% at (pH = 11, catalyst loading = 1.3 g TiO_2/L, and H_2O_2 =200 mg/L). Empirical correlations were suggested for the photoreduction of Cr (VI) and Cu (II) ions as functions of the studied operating parameters with correlation coefficients of 0.946 and 0.948, respectively.*

Keywords- *Photocatalysis; solar light; metallic ions reduction; synthetic wastewater; reaction kinetics*

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1. Introduction

Currently we are living in an environment of hazardous metal ions due to industrial activities. Copper is generally not harmful to humans at low concentration in the range of μg mL^{-1}. However, copper can be toxic to aquatic plants and some fish at concentrations even less than 1 μg mL^{-1} [1]. It is well known that chromium is widely used in several industrial processes such as metal plating and paint making. In most countries, Cr (VI) is in the list of highly harmful pollutants due to its acute toxicity and high mobility in water. The toxicity of Cr (VI) is one hundred times higher than that of Cr (III) [2].Literature are rich in studies of heavy metals removal from wastewater by conventional methods, such as by using adsorption [3], biodegradation [4], and membrane separation. These are simple and non-destructive, i.e., it is only transferring the ions from the solution phase into another phase, which leads to further environmental problems. Recently photocatalysis has evolved as an alternative technique for treating wastewater containing hazardous metals and organic compounds [5]. The reduction strength of photocatalysis has been used to recover expensive metals from industrial effluent, such as gold, platinum and silver [6]. Chen et al. [7] reported that the process of removal or recovery of dissolved metal ions in wastewater couples UV-light with particles acting as catalyst and is based on the reduction by the photogenerated of electrons. It is well known that when a semiconductor is photo-exited by ultraviolet light with having energy more than the bandgap energy of the semiconductor, an electron/hole pairs is produced in the semiconductor. Reduction by the photo-produced electrons happens simultaneously with oxidation by the photo-produced holes during the photocatalysis. In photocatalysis the rate of reaction is highly affected by the rate of recombination photo-produced electrons and holes [8,7]. The effects of different additives such as acetic acid, citric acid, salicylic acid on the reduction of chromate in synthetic wastewater were studied by [9] using photocatalysis. They reported that the type of organic play an effective role in measuring the rate of chromate reduction.
Cho et al. [10] studied the removal of toxic metal such as Cd, Cr, Cu, Hg, Ni, Zn under natural solar light using circular reactor. They reported that the removal of each metal was more than 90% in the presence of TiO_2/solar light. Wahyuni et al. [11]

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reported that the reduction of Cr(VI) and Cu(II) ions is promoted by photocatalyic which occurs by trapping the generated electrons from the photon-exiting of water and TiO_2 catalyst [3], as shown by eqns. (1), (2), and (3).

$$TiO_2 + hv \longrightarrow TiO_2^* + e^- + h^+ \quad (1)$$

$$Cu^{2+} + 2\,e^- \longrightarrow Cu^o \ (E^o = +0.34\ V) \quad (2)$$

$$Cr_2O_7^{=} + 6e + 14\,H^+ \longrightarrow 2\,Cr^{3+} + 7\,H_2O \ (E^o = +1.50\ V) \quad (3)$$

In present study the effects of pH, amount of catalyst, and H_2O_2 concentration on reduction of Cr (VI) and Cu (II) ions in synthetic wastewater were investigated against exposure time. The kinetic parameters of metal ions reduction were also studied.

2. Materials and Methods

I. Materials

Chemicals and reagents used in the present wok are listed in Table 1.

II. Experimental setup and procedure

In a glass cylindrical batch reactor (500 ml), the reactants were charged, well mixed by a magnetic stirrer, and are left to react for a certain period. The effects of the pH, initial metal ion concentration, amount of catalyst, H_2O_2 loading on reduction of metal ions were investigated and optimal conditions were found out. Experiments on photo-degradation of metal ions using TiO_2 under direct and indirect irradiant sunlight, respectively, were carried out.

III. Analytical methods

All samples were drawn by a 2-ml syringe at 15-minutes time interval, centrifuged by Table Top Centrifuge (PLC – Series/ china), and filtered by Millex-HA membrane filter (Millipore, 0.25 μm) before analysis. The filtrate was analyzed for metal ion concentrations by UV-spectrophotometer Model UB-1201 PC. Calibration curves (Figures 1 and 2) were generated for different concentrations of Cr (VI) ions (5, 10, 20, 50, 100.150, 200 mg/L) and Cu (II) ions (5,10, 20, 50,100, 150, 200 mg/L) vs. light absorbency, respectively.

IV. Preparation of synthetic wastewater

0.11 g of $K_2Cr_2O_7$ was dissolved into 2 L RO water to prepare the aqueous solution with a Cr (VI) concentration of 20 mg L^{-1}.

A solution of 1000 mg/L of Cu (II) was prepared by adding 4.0 g of CuSO4 to 1000 mL of RO water. 0.01 M EDTA was added for formation of a complex to easily detect by UV-Spectrophotometer.

V. Experimental Design

For design the experiments, a factorial method was used, because of its efficacy in finding the interaction between the selected real variables of the studied system [12]. Table 2 lists the real variables (F) and their levels (L) used for experimental design of the present work.

Table 1: Chemicals and reagents of the present study

no.	Item	Specification	Supplier
1	TiO_2 nanocatalyst	Crystal phase 80% anatase, average size 20 nanometer, surface area = 160 m^2/g.	ZXC, China
2	Copper Sulfate	Anhydrous powder, Purity= 99 wt%	Merck Chemicals
3	Potassium Chromate	Crystalline powder, Purity = 99 wt%	Bayer Chemicals
4	EDTA	Liquid, Purity= 98% min.	Fluka Chemicals
5	Hydrochloric acid	Liquid, 37 wt%	Sigma Aldrich
6	Caustic Soda	Pellet, Purity=98wt% min	Sigma Aldrich
7	RO water	(Conductivity <10, μS cm^{-1}, Cl^- = 0.7–0.8 mg L^{-1}, NO_3^- = 0.5 mg L^{-1}, organic <0.5 mg L^{-1}).	Auto-analysis Laboratory, Chemical Engineering Department

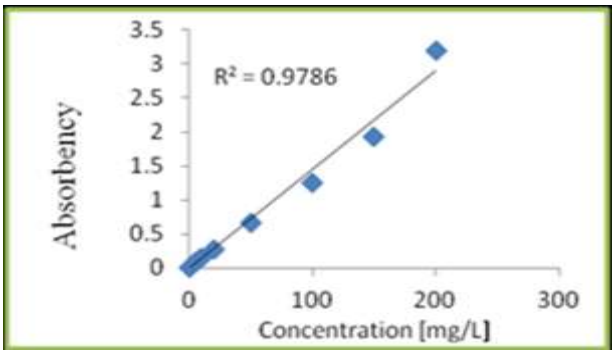


Figure 1: Calibration curve of Cr (VI) ions in Water

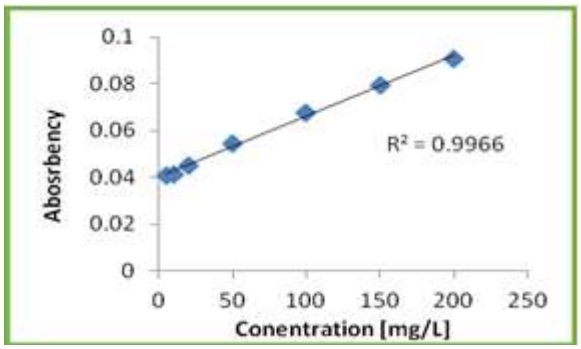


Figure 2: Calibration curve of Cu (II) ions in Water

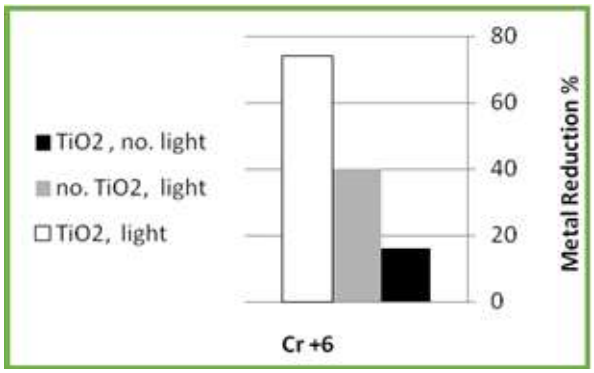
Table 2: Selected levels and factors

Level no.	pH	Catalyst load (g/L)	H_2O_2 load (mg/L)
1	3	0.9	50
2	5	1.3	100
3	7	1.7	200
4	9		300
5	11		

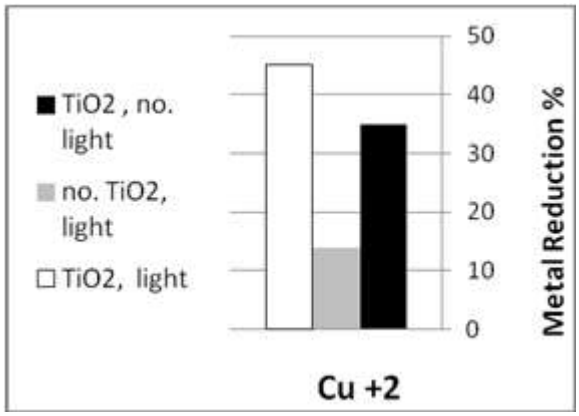
3. Results and discussion

I. Blank experiments

Figure 3 (a and b) illustrate the influence of dark, light, and TiO_2 on metal ion removal of 50 mg/ L of each Cr (VI) and Cu (II), respectively, during the 90 min of illumination time. As can be seen in Figures 3a and 3b, the present results confirmed that during the photocatalytic step a main reduction is occurred.



(3.a): removal efficiency of Cr (VI) ion



(3.b): removal efficiency of Cu (II) ion

Figure 3: Influence of various operating conditions on metal ions removal

II. Effect of pH on the photocatalytic removal

Figures 4 and 5 show the degree of reduction for Cr (VI) and Cu (II) ions at the various pH keeping other parameters unchanged (H_2O_2 = 50 mg/L, TiO_2 = 0.9 g/L), respectively. As can be illustrated in Figure 4, the rate of reduction of chromate ions gradually decreased as pH increased, this may be attributed to the reduction of adsorption of dichromate ions on the surface of the catalyst, by increasing the solution pH; further increase of solution pH causes the removal of Cr (VI) decreased sharply. This may be attributed to the production of Cr $(OH)_3$ which may inhibit the penetration of UV- light into solution, consequently less hydroxyl radicals would be generated for photocatalytic reduction. According to Figure 4 at pH 3 and 7, the corresponding removal of Cr (VI), after 120 min are 93% and 66%, respectively. While at pH 11 the corresponding removal of Cr (VI) is 40%, respectively. The trend of our results agree well with the findings of [13, 14, 15, 16]

As can be observed in Figure 5, the Cu^{+2} ion reduction is increased as pH increased from 3 to 7. The trend of the effect of solution pH could be explained based on the metal ion characteristics and the surface of TiO_2. As the solution pH increased from 3 to 7, the wetted surface of TiO_2 is found as $TiOH_2^+$, in this case hydroxyl radicals ($^{\bullet}OH$) would not be easily to release, as well as cations is being difficult to adsorb. Increasing solution pH more than 7 the surface of TiO_2 changes to TiOH, which is easier to provide electrons and $^{\bullet}OH$ radicals as well as to adsorb the cations. This condition results in the increase of the removal effectiveness of the metal ions. At pH higher than 7, an increase in the degree of Cu(II) removal from the solution is observed due to formation of $Cu(OH)_2$ precipitate. Consequently, during the analysis of metal ions in

the solution are not detected. As a result the higher removal at higher pH is not caused by precipitation. According to Figure 5 at pH 3 and 7, the corresponding removal of Cu (II), after 120 min are 80% and 88.5%, respectively. While at pH 9 and 11 the corresponding removal of Cu (II) is 90 and 92%, respectively. The present results agree well with the findings of [17, 5].

III. Effect of catalyst loading

The loading of TiO_2 was varied from 0.9 to 1.7 g/L in the solution to investigate its influence on the efficiency metallic ion reduction under solar-UV light. Figures 6 and 7 plot the degree of reduction for Cr (VI) and Cu (II) ions at the various TiO2 loading keeping other parameters unchanged (H_2O_2 = 50 m g/L, pH= 7), during 120 min of illumination time, respectively. As can be illustrated in Figures 6 and 7, the rate of ion reduction increased steadily at the early period of experimental run while the rate of reduction became slower at the subsequent period. This may be attributed to the concentration of metallic ions
which are higher at the early stages of the photocatalysis resulted to higher reaction rate. However, metallic ions concentration decreased as the rate of reaction proceeds. Figures 6 and 7 illustrate a positive relationship between TiO_2 loading and the reduction of Cr (VI) and Cr (II); this behavior is almost attributed to the increase of metallic ions adsorption on catalyst surface with However the reduction rate decreased as the catalyst loading increased from (1.3 to 1.7) g/L, this phenomenon may be explained by the light scattering, caused by the lightproof of high concentration of suspended catalyst [18, 20]. It is worth notice that the efficiency of ion reduction for Cr (VI) at 120 min was 92% and 94% at 1.3 g TiO_2/L and 0.9 g TiO_2/L, respectively.

IV. Effect of H_2O_2 loading

Figures 8 and 9 plot the reduction of Cr (VI) and Cu (II) ions against H_2O_2 loading in solution keeping other parameters unchanged during the experimental time, respectively. To investigate the influence the loading of hydrogen peroxide on the reduction of Cr (VI) and Cu (II) ions various concentrations of H_2O_2 (50, 100, 200, and 300 mg/L) were used. As can be shown in these Figures, the ion reduction promoted with increasing the H_2O_2 loadings. However, the reduction of ions was slow at low H_2O_2 loading, because the generation of ($^{\bullet}$OH) radicals was not sufficient, this may be due the role of H_2O_2 to capture the electrons retarding the recombination of electron–hole and so enhance the probability of generation more ($^{\bullet}$OH) radicals on the catalyst surface. Moreover, as can be observed in Figure 8a, the rate of ion reduction becomes less as the loading of hydrogen peroxide increased more than 100 mg/L. This may be attributed to the, excess addition of hydrogen peroxide which generates high amounts of hydroxyl radicals. However, the excess free radicals would react with the excess of H_2O_2 rather than with the metal ions. The same trend could be found in Figure 8b. As can be shown in Figure 8b, a remarkable increase on the reduction of copper ions occurs when at a loading of H_2O_2 equal (200 mg/L). At 120 min. of irradiation, the reduction of Cr (VI) ion was (97.0%) when the H_2O_2 concentration was increased to 100 mg/L. For Cu (II), the reduction was 97.7% as the loading of hydrogen peroxide was 200 mg/L but the reduction of Cu (II) ions decreased to 96.9% as H_2O_2 loading increased to 300 mg/L. Present results agree well with the findings of [21, 22]. Ku and Jung [23] reported that H_2O_2 play a dual mechanism in photocatalysis, it acts as an electron acceptor and may decompose to generate ($^{\bullet}$OH) radicals

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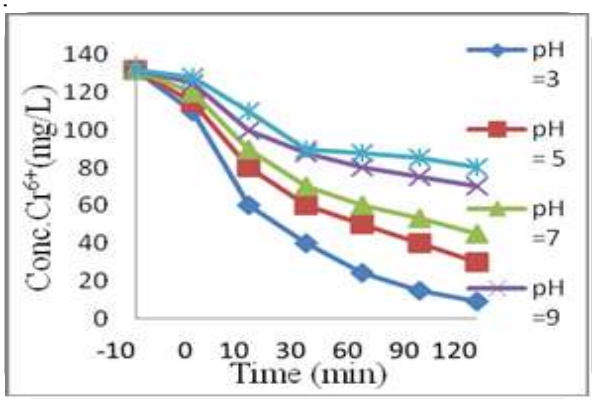


Figure 4: Effect of pH on the photocatalytic removal

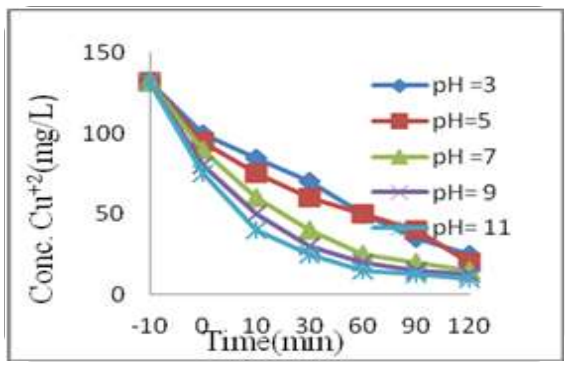


Figure 5: Effect of pH on the photocatalytic removal

of Cr^{+6} ion of Cr^{+6} ion

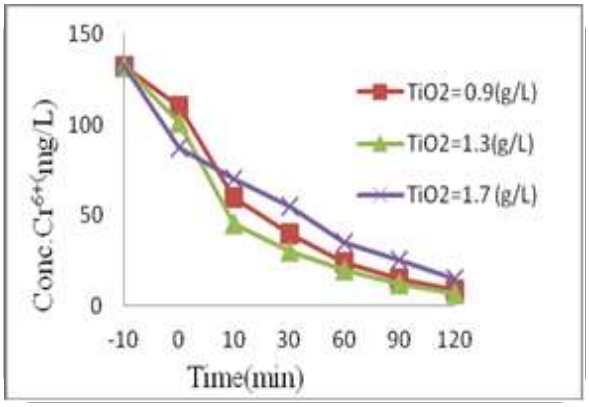


Figure 6: Effect of TiO_2 catalyst loading on Cr (VI) ions removal

of Cu^{+2} ion

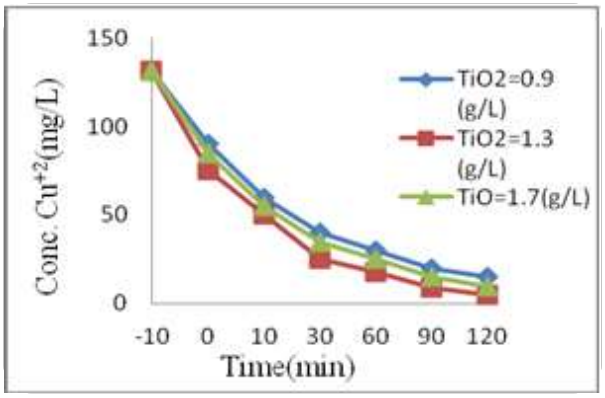
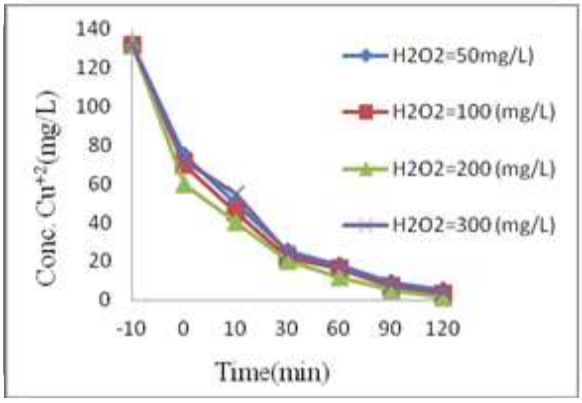
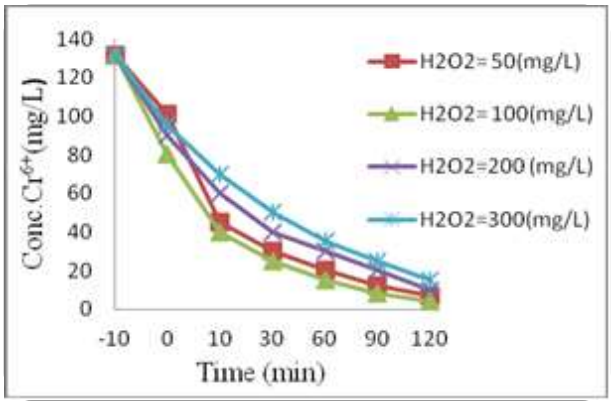


Figure 7: Effect of TiO_2 catalyst loading on Cu (II) ions removal



(a)



(b)

Figure 8: Effect of H_2O_2 loading on ions removal (a) Cr(VI), (b)Cu (II*)*

4- Mathematical Correlations

Based on the experimental results, the following power law based correlations were proposed to predict the removal rate of the metallic ions in synthetic wastewater for the studied ranges of operating parameters of pH, H_2O_2 loadings, catalyst loadings, and instantaneous time of measurements.

For Cr^{+6} removal:

$$\%R_{Cr+6} = a_o [pH]^{a1} [C_{H2O2}]^{a2} [C_{TiO2}]^{a3} [\frac{t\ ins}{t\ tot.}]^{a4} \quad (4)$$

For Cu^{+2} removal:

$$\%R_{Cr+6} = b_o [pH]^{b1} [C_{H2O2}]^{b2} [C_{TiO2}]^{b3} [\frac{t\ ins}{t\ tot.}]^{b4} \quad (5)$$

where R_{Cr+6} and R_{Cu+2} are the percentage removal of Cr_{+6} and Cu_{+2}ions, respectively.

C_{H2O2} is the concentration of H_2O_2 in mg/L. C_{TiO2} is the catalyst loading in mg/L. t_{ins} is the instantaneous time of measurement in min. t_{tot} is the total time of each experiment in min. The coefficients of equations 4 and 5 were estimated using regression analysis technique.The following equations for removal of Cr (VI) and Cu (II) were obtained from the two equations above:

For Cr (VI):

$$\%\ R_{Cr+6} = 246.14[pH]^{-0.657} [C_{H2O2}]^{-0.0646} [C_{TiO2}]^{-.0396} [\frac{t\ ins}{t\ tot.}]^{0.2976} \quad (R^2 = 0.946) \quad (6)$$

For Cu (II):

$$\%\ R_{Cr+6} = 29.012[pH]^{0.195}[C_{H2O2}]^{0.187}[C_{TiO2}]^{0.002} [\frac{t\ ins}{t\ tot.}]^{0.226} \quad (R^2 = 0.948) \quad (7)$$

5. Conclusions

The present work was devoted to investigating the feasibility of utilizing solar light to degrade Cr (VI) and Cu (II) ions in synthetic wastewater. The effect of the key process parameters on the quality of product was studied by varying the pH (3, 5, 7, 9, and 11), H_2O_2 (50, 100, 200, and 300 mg/L) and TiO_2 loading (0.9, 1.3, and 1.7 g/L). Experimental results revealed that after 120 min of solar illumination the highest reduction of Cr (VI) ions was 97.0% obtained under (pH = 3,

catalyst loading = 1.3 g TiO2/L, and H_2O_2 =100 mg/L) and for Cu (II) ions the highest reduction of was 97.7% under (pH = 11, catalyst loading = 1.3 g TiO2/L, and H_2O_2 =200 mg/L). Mathematical correlations were proposed for the reduction of Cr (VI) and Cu (II) ions as functions of the studied operating parameters with correlation coefficients of 0.946 and 0.948, respectively.

Acknowledgments

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References

[1] R. Hamid and M. Rafat, "Simultaneous Determination of Nickel (II) and Copper(II) by Second-Derivative Spectrophotometric Method in Micellar Media," Journal of the Chinese Chemical Society, Vol. 54, 157-164, 2007.

[2] G. Cappelletti, C. L. Bianchi, and S. Ardizzone, "Nano-titania assisted photoreduction of Cr(VI). The role of the different TiO_2 polymorphs," Journal of Applied Catalysis: B, Vol. 78, No. 3-4, 193–201, 2008.

[3] P.J.M. Carrot, R. Carrot, J.M.V. Nabais, and P. Ramalho, "Influence of Ionization on the Adsorption of Aqueous Zinc Species by Activated Carbon," Elsevier Science, Vol. 35, 403-410, 1997.

[4] T.Y. Kim, S.K. Park, S.Y. Cho, H.B. Kim, Y. Kang, S.D. Kim, and S.J. Kim, "Adsorption of Heavy Metals by Brewery Biomass," Korean Journal of Chemical Engineering, Vol. 22, No. 1, 91-98, 2005.

[5] S. Sarika, K. C. Barick and D. Bahadur, "Functional Oxide Nanomaterials and Nanocomposites for the Removal of Heavy Metals and Dyes," Journal of Nanomaterials and Nanotechnology, Vol. 13, 1-8, 2013

[6] D.F. Ollis, E. Pelizzetti, and N. Serpone, "Photocatalyzed destruction of water Contaminants," Environmental Science and Technology, Vol. 25, 1522-1529. 1991.

[7] D.W. Chen, M. Sivakumar, and A.K. Ray, "Heterogeneous photocatalysis in environmental remediation," Developmental Chemical Engineering and Mineral Processes, Vol. 8, No. (5/6), 505-550. 2000.

[8] A. Mills and S. Le Hunte, "An overview of semiconductor photocatalysis," Journal of Photochemical Photobiology. A: Chemistry, Vol.108, 1–35. 1997.

[9] M.R. Prairie, L.R. Evans, B.M. Stange, and S.L. Martinez, "An investigation of TiO_2 photocatalysis for the treatment of water contaminated with metals and organic chemicals," Journal of Environmental Science Technology, Vol. 27, 1776-1782, 1993.

10] I.H. Cho, T J. Park, H.Y. Kim, K.D. Zoh and H.K. Lee, "A study on the removal of toxic metal-EDTA complex using solar light/TiO2 system," Journal of Water Science and Technology: Water Supply, Vol. 2, No. 1, 299–304, 2002.

[11] E.T. Wahyuni, and S. Sudiono, "The Influence of Organic Acids and Heavy Metals on The Photoreduction of Cr(VI) Vatalyzed by TiO2 Suspension," Journal of Chemical Engineers, Vol. 5, 657-662, 2011,

[12] A.A. Aldalawi, "Hydrodynamic characteristic effect of foam control in a three-phase bubble column," MSc. Thesis, Department of Chemical Engineering, University of Technology, Baghdad, Iraq, 2010.

[13] S.F. Chen and G.Y. Cao, "Study on the photocatalytic reduction of dichromate and photocatalytic oxidation of dichlorvos," Journal of Chemosphere, Vol. 60, No. 9, 1308–1315, 2005

[14] M.M. Chih, S.S.Yung, and H.L. Po, "Photoreduction of Cr(VI) Ions in Aqueous Solutions by UV/TiO2 Photocatalytic Processes," International Journal of Photoenergy: Special section p1, No. 1-7,2012.

[15] J. Saien A. Aziz, "Simultaneous photocatalytic treatment of Cr (VI), Ni(II) and SDBS in aqueous solutions: Evaluation of removal efficiency and energy consumption," Journal of American Institute of Chemical Engineers, E 95, 114–125,2015.

[16] M. Malakootian, and F. Mansuri, "Hexavalent chromium removal by titanium dioxide photocatalytic reduction and the effect of phenol and humic acid on its removal efficiency," Int J Env Health Eng , 4(19), 1-8,2015.

[17] E.T. Wahyuni, N.H. Aprilita, H. Hatimah, A.M. Wulandari and M. Mudasir, "Removal of Toxic Metal Ions in Water by Photocatalytic Method," American Chemical Science Journal, Vol. 5, No. 2, 194-201, 2015.

[18] A.H.C. Chan, C.K. Chan, J.P. Barford, and J.F. Porter, "Solar photocatalytic thin film cascade reactor for treatment of benzoic acid containing wastewater," Water Research, Vol. 37,1125 1135. 2003.

[19] W.Z.Tang, Z. Zhang, and H. Ann, "TiO_2/UV Photodegradation of azo dyes in aqueous solutions," Environmental Technology, Vol. 18, 1-12. 1997.

[20] J. Grzechulska-Damszel, M. Tomaszewska, and A.W. Morawski, "Integration of photocatalysis with membrane processes for purification of water contaminated with organic dyes," Desalination, Vol. 241, 118-126, 2009

[21] Y. Wang, and C.S. Hong, "Effect of hydrogen peroxide, periodate and persulfate on photocatalysis of 2-chlorobiphenyl in aqueous TiO_2 suspensions," Journal of Water Research, Vol. 33, 2031-2036. 1999.

[22] Z. Barhon, N. Saffaj, A. Albizane, M. Azzi, R. M., Mamouni, and M. El Haddad, "Effect of modification of zirconium phosphate by silver on photodegradation of methylene blue," Journal of Material Environmental Science, Vol. 3**,** 879-884, 2012

[23] Y. Ku and I. L. Jung, "Photocatalytic reduction of Cr(VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide," Journal of Water Research, Vol. 35, No. 1, 135–142, 2001.

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