Synthesis and Characteristic Study of Composite Zinc Oxide and Functionalized Activated Carbon with Investigation of its Adsorption Ability: A Kinetic Study

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ABSTRACT

This work involves preparation of activated carbon (ACs) that is derived from Iraqi zahdy date palm seeds (IZDPS). These ACs then were functionalized using HNO₃ as an oxidizing agent to yield functionalized activated carbons (FACs). The obtained FACs then combined with zinc oxide nanoparticles to produce activated carbon/zinc oxide (AC/ZnO). The obtained composites were investigated using different methods such as X-rays diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and specific surface area (BET). The adsorption activity of these materials was conducted by following removal of Celestin blue B (CBB) dye from simulated textile wastewaters. Different reaction conditions were investigated such as pH effect, the effect of both contact time and the mass of the used adsorbent on the efficiency of dye removal. Removal of CBB dye over the suspension was investigated by measuring the absorbance of supernatant liquid at a wavelength of 644 nm. Adsorption isotherms were investigated using both by Langmuir and Freundlich adsorption isotherms and the results were more fitted with Langmuir model. The kinetics of adsorption was investigated, and the obtained results were fitted with pseudo second order kinetics model.

Keywords: Textile dye wastewaters, Activated carbon/ZnO, Dyes removal., Celestin blue b dye, Adsorption processes.

INTRODUCTION

In our modern world, organic dyes become main source for pollution of our environment. These dyes are involved in very wide range of industrial processes. In this context, textile dyes play main role in this proposed environmental pollution. These dyes are existed in high concentration levels with textile effluents wastewaters. This type of wastewaters normally shows highly colored industrial effluents and in most cases these dyes having rigid structure with high toxicity. Due to this point these dyes are too stable under ambient conditions. Generally, passing of these dyes from effluents to the soil or to the ground water or to the rivers or any other type of water can effect on both human,
living organisms and plant life. Due to these observations, removing or at least reducing their levels in polluted wastewaters becomes a big challenge especially in industrial countries\textsuperscript{4,5}.

In this context, different methods and techniques are applied since a long time to do this aim and these are including adsorption processes, biological methods, physical and chemical methods\textsuperscript{6}. These methods are still not effective in dye removal from effluents wastewaters and these are not too easy to be performed as well as to its high cost in many cases\textsuperscript{6,7}. Due to these draw back points, researchers have been looked for more developed methods to achieve this aim. In this manner production of adsorbent materials with low cost is probably alternative methods to do this aim. In this context producing activated carbons (ACs) from ambient agricultural wastes can play important role in treatment of polluted wastewaters with dyes as these materials are highly available and can be processed with very low cost. Besides that, these ACs can be re-used many times with just very simple activation processes\textsuperscript{7,8}. To enhance adsorption ability of ACs it can be combined with photocatalyst such as zinc oxide\textsuperscript{9-12}. However, a composite of AC/ZnO can be effective system due to synergistic effect that is exposed to occur between ZnO and AC particles which can enhance its adsorption activity. Synergistic effect between ACs and ZnO particles can arise from high porosity and high specific surface area of ACs and these factors would give a role of AC in wide separations of ZnO particles\textsuperscript{13,14}. High porosity and specific surface area of the proposed composite can lead to increase its adsorption efficiency and hence high efficiency of dye removal from wastewaters are expected\textsuperscript{15}. Introduction of some functional groups on surface of ACs can enhance its surface properties. The presence of these functional groups can lead to improve catalytic properties of the binary system (AC/ZnO)\textsuperscript{16,17}.

The current study presents synthesis composites of AC/ZnO and study adsorption ability for these materials in concern with removal of CBB dye. The study also would involve investigating of different adsorption conditions as well as study kinetics of adsorption via applying both of presudo first and second order kinetics models.

**EXPERIMENTAL PART**

**Used chemicals:** Celestine Blue B dye was used as a polluted textile dye model. This dye has a molecular formula of $C_{17}H_{18}ClN_3O_4$ with a molecular weight of 363.80 g.mol$^{-1}$. This dye was purchased from Sigma Aldrich Company (80%). Zinc oxide was purchased from Fluka company (99.5%), it has a band gap energy of 3.37 with a molar mass of 81.401 g/mol. with a density of 5.606 g/cm$^3$\textsuperscript{18}. 
Synthesis of activated carbon (ACs): The used activated carbons was synthesized using Iraqi zahdi date palm seeds (IZDPS) with KOH in a chemical activation process. Synthesis details were reported in our previous published article19.

Synthesis of composites of AC/ZnO: A simple evaporation and drying process was used in preparation of composites of AC/ZnO (10%). According to this method, one gram of ZnO was suspended in 100 mL of DW with sonication for 30 minutes. In another flask, a sample of ACs was suspended in 20 mL of DW and was sonicated for 15 minutes. Then AC sample was added to ZnO suspension under continuous stirring and the resultant mixture was heated at 80 °C until the complete evaporation of water. The remaining solid was dried for overnight in an oven at 110 °C to yield AC/ZnO composite20.

Determination of surface area of activated carbons and its composites with ZnO: Specific surface area for both single and composites materials (AC/ZnO samples were investigated according to the procedure that was reported according to Saers, method21.

Characterization of the composite of AC-ZnO: A composite of FAC/ZnO were investigated using different techniques such as specific surface area (BET), powder X-rays diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR).

Adsorption studies: Adsorption study was carried out using a shaker water-bath which enable controlling on both temperature and stirring rate for all experiments. In this part, all experiments were carried out using aqueous solutions of CBB dye (50 ppm, 30 mL) in a conical flask. To this solution a required amount of adsorbent (ZnO, AC and FAC/ZnO), was suspended with dye solution. Adsorption processes were conducted for one hour for each run and experiments were carried out under ambient atmospheric conditions with a continuous stirring. Periodically, samples of 2 mL at each ten minutes were withdrawn. Then samples were centrifuged sometimes to remove fine particles from reaction mixture. Then optical density of the liquid was recorded at 642 nm using UV-Vis Shimadzu 1650 PC-UV-visible Spectrophotometer. The percentage of dye removal (R%) was calculated using the following relationship22,23.

\[ R\% = \frac{c_i - c_f}{c_i} \times 100 \]

Whereas, Ci refers to the initial concentration of CBB dye, Cf, refers to the final concentration of the dye after one hour of adsorption process.
RESULTS AND DISCUSSION

Specific surface area of the binary composite materials:

The specific surface area of each of AC, ZnO and, AC/ZnO were calculated via applying Saers, method\(^{24}\). The obtained BET specific surface areas are shown in Table 1.

| Catalyst       | ZnO | AC | AC/ZnO |
|----------------|-----|----|--------|
| Specific surface area m\(^2\)/g. | 40  | 910| 905    |

Specific surface areas measurements showed that ACs exhibited almost high specific surface area this can be attributed to nature of its porous structure with high porosity and vacancies. From obtained results, it was found that AC-ZnO showed some reduction in surface area in comparison with naked AC. This reduction in surface can be related to the nature of the prepared composites (AC/ZnO) in comparison with neat AC and this probably arises from strong interaction between functional groups at the surface of AC and that at the surface of zinc oxide and this interaction can lead to some reduction in the final surface area of the composite\(^{24,25}\).

X-rays diffraction (PXRD) for ZnO and AC/ZnO: XRD patterns for each of neat ZnO and AC/ZnO are presented in Figure 1 and these patterns showed that ZnO have crystalline structure which means that presence of AC doesn't affect significantly on its crystallite. ZnO nanoparticles have a crystalline structure with characteristic peaks at 2 Theta equal to 31.79, 34.45, 36.26, 47.33, 51.30, 56.26, 62.35, 65.84, 67.48, and 68.41\(^{26,27}\). The crystal size was calculated using Scherer's equation and it was around 68 nm. On other hand, XRD patterns of AC-ZnO are almost similar to that of neat ZnO. This means that combination of AC with ZnO at this level around (10%) doesn't affect the crystalline structure of ZnO.
 Fourier transform infrared spectroscopy (FTIR): FTIR spectra of the prepared materials are shown in Figure 2. These spectra showed a broad peak around 3250–3550 cm\(^{-1}\), this peak is due to the stretching vibration of hydroxyl group at the surface of both AC and zinc oxide. Weak peaks around 400-600 cm\(^{-1}\) are related to the characteristic peak of (Zn-O) bond. FTIR spectra for AC/ZnO showed a broadening in FTIR spectra for neat ZnO. In addition to that, there are some peaks that can be related to the AC in range of 1350–1710 cm\(^{-1}\). The peak around 1600 cm\(^{-1}\) is assigned to C=O bond. The peak around 1600 cm\(^{-1}\) is related to the vibration modes of aromatic rings in coupling with carbonyl groups at the surface of composite. The peak around 1000 cm\(^{-1}\) is related to stretching modes of C=O bond. A weak broad band around 3000 cm\(^{-1}\) is assigned to C=C bonds. The band around 800 cm\(^{-1}\) is related to vibration of the C-H bending mode. The bands around 2500 cm\(^{-1}\) are assigned to stretching modes of hydroxyl groups. The peaks around 3500 to 4000 cm\(^{-1}\) are related to the stretching modes of surface hydroxyl OH groups. FTIR spectra for ZnO sample, are almost similar to the peaks of AC/ZnO. In addition to that, FTIR spectra for AC/ZnO showed some peaks around 1000-1600 cm\(^{-1}\) and these peaks are attributed to cyclic ether and quinone.
**Removal of CBB dye by adsorption over AC-ZnO:** To investigate adsorption ability of AC, ZnO and AC-ZnO, a series of experiments were performed to choose the best adsorbent under the same adsorption conditions and for a period of one hour for adsorption time. Removal efficiency was calculated using the following relation:

\[
\text{Removal\%} = \frac{A_o - A_t}{A_o} \times 100
\]

Whereas \(A_o\) is the absorption at time equal to zero and \(A_t\) is the adsorption at any time after starting adsorption. From the obtained results, it was found that AC-ZnO was the best one of these adsorbents which showed removal efficiency of 95.7% of CBB after one hour at 293 K and at a pH = 7. The obtained results are listed in Table 2 and are plotted in Figure 3.

**Table 2:** Removal percentage of CBB dye over different adsorbents under applying same adsorption conditions.

| Time of adsorption (min) | ZnO  | AC   | AC-ZnO |
|--------------------------|------|------|--------|
| 0                        | 0    | 0    | 0      |
| 10                       | 26.42| 54.77| 62.03  |
| 20                       | 54.64| 61.78| 68.15  |
| 30                       | 82.16| 89.31| 94.52  |
| 40                       | 83.43| 90.31| 95.41  |
| 50                       | 86.87| 93.21| 95.66  |
| 60                       | 88.4 | 93.22| 95.7   |

**Fig. 3.** Removal of CBB dye over AC, ZnO and AC-ZnO at 293 C using 0.05 g. of each adsorbent at pH=7.

From the results that are presented in Table 2 and Figure 3, it can be seen that the best removal efficiency by adsorption for the dye was obtained when use AC/ZnO as an adsorbent and it was around of 96% after one hour of adsorption time. This probably due to high surface area with a high porosity of the composite (AC-ZnO) in comparison with the single materials (AC alone and ZnO alone). This result also can be attributed to the synergistic effect of AC and ZnO. These factors would lead to
increase adsorption ability of the composite which gives higher removal efficiency for the used composite in comparison with singly used materials\textsuperscript{31,32}.

**Effect of catalyst weight on Adsorption of CBB over AC/ZnO composite:**

After investigation the best adsorbent (AC-ZnO) from the previous part. Another study was performed to investigate the effect of the mass of AC-ZnO on adsorption of the dye. A series of experiment was performed using different masses of the adsorbent, 0.05, 0.10, 0.20 and 0.25 g., at 293 C and at a pH =7 for one hour of each run. The obtained results are presented in Table 3 and Figure 4.

**Table 3: The effect of mass of AC-ZnO on adsorption of CBB dye**

| Weight of the used AC/ZnO (gram) | Time of adsorption (min.) | 0.05 | 0.10 | 0.20 | 0.25 |
|---------------------------------|---------------------------|------|------|------|------|
|                                 |                           | 0.05 | 0.10 | 0.20 | 0.25 |
| 10                              |                           | 62.03| 68.15| 74.64| 76.05|
| 20                              |                           | 68.15| 74.52| 75.79| 77.07|
| 30                              |                           | 94.52| 95.21| 96.4 | 97.78|
| 40                              |                           | 95.41| 95.41| 97.03| 97.91|
| 50                              |                           | 95.66| 95.97| 97.28| 97.93|
| 60                              |                           | 95.7 | 96.21| 97.45| 98.43|

![Figure 4](image-url)  

**Fig. 4.** Effect of mass of AC-ZnO on CBB dye adsorption at 293 K and pH=7 for adsorption time of one hour.
From the obtained results, it can be seen that the adsorption efficiency of dye was increased with the increase of mass of AC-ZnO and the best result recorded at 0.25 g., in this case removal efficiency was around 98.4% at 293 K. This result arises from the increase of the available of adsorption sites with the increase of mass of adsorbent, these adsorption sites at the surface contribute in removing of dye molecules from the bulk solution to be adsorbed at the surface\textsuperscript{33,34}.

The effect of pH on CBB dye removal by adsorption over AC/ZnO: To investigate the effect of pH of adsorption system on removal of CBB dye over a suspension of AC/ZnO, a series of experiments were performed. In this context, 0.25 g. of the adsorbent were suspended in 30 mL of dye solution (50 ppm) at 293 K. All runs were carried out under the same reaction conditions, with change of pH of reaction mixture and herein three different pHs values were applied and these were 3, 4 and 9. The obtained results of CBB dye removal by adsorption over AC/ZnO are presented in Table 4 and Figure 5.

Table 4: The effect of pH of reaction mixture on CBB dye adsorption over AC-ZnO suspension.

| Time of adsorption(min.) | pH = 3 | pH = 4 | pH = 9 |
|-------------------------|--------|--------|--------|
| 0                       | 0      | 0      | 0      |
| 10                      | 66.00  | 76.05  | 78.00  |
| 20                      | 69.00  | 77.07  | 82.00  |
| 30                      | 94.39  | 97.78  | 98.87  |
| 40                      | 94.5   | 97.91  | 98.89  |
| 50                      | 94.77  | 97.93  | 98.91  |
| 60                      | 94.9   | 98.43  | 99.03  |
The effect of pH of reaction mixture on adsorption of CBB dye on AC-ZnO was investigated by performing a series of experiments using 0.25 g. of the adsorbent at 293 K. These experiments were conducted under three different pHs, 3, 4 and 9. The obtained results of dye removal are presented in Table 4 and Figure 5. From the obtained result in this part, it can be seen that the efficiency of dye removal adsorption was increased slightly with increase of pH from acidic into basic values and the efficiency of dye removal by adsorption was reached the optimum value around 98% at basic medium (pH=9). This result can be assigned to enhance in adsorption ability of dye molecules over AC/ZnO surface in basic medium due to increase attraction between dye molecules and negatively charged surface of the composite at this basic medium (pH=9). In converse to that, and at acidic medium the surface would have positive charge nature which leads to increase repulsion between surface and dye molecules. This effect leads to reduce adsorption ability of dye molecule on adsorption sites at AC/ZnO surface and this leads to reduce the efficiency of dye removal under acidic medium in comparison with high basic medium.

**Adsorption isotherms:** Adsorption isotherms for adsorption of CBB dye over a suspension of AC/ZnO at 293 K was investigated using both of Langmuir and Freundlich adsorption isotherms. It is known that Langmuir adsorption model, based on formation of homogeneous monolayer of the adsorbed dye molecules at the surface of the adsorbent. Freundlich adsorption model applies for physical adsorption and based on formation of multilayers of adsorbate at the surface. The following equations are used to investigate both of Langmuir and Freundlich adsorption isotherms.

\[
\frac{1}{qe} = \frac{1}{qm} + \frac{1}{KLqm} Ce \\
\log qe = \log Kf + \frac{1}{n} \log C
\]

context, \(qe\) is the amount of adsorbed dye molecules on AC-ZnO in (mg/g); \(qm\) is the capacity of monolayer adsorption of CBB dye in (mg/g); \(KL\) is Langmuir adsorption constant in (L/mg); \(Ce\) is the dye concentration at equilibrium case in (mg/L); both \(Kf\) and \(1/n\) are referred to the constants of the Freundlich adsorption isotherm. Maximum adsorption capacity for AC-ZnO can be calculated using Langmuir equation under applying reaction conditions, temperature of temp. 20 °C, pH 7.0, and the
initial concentration of CBB dye 50 ppm. The doses of the used AC-ZnO ranged from 0.05, 0.10, 0.20 and 0.25 g. The results of adsorption isotherm constants and R² are presented in Table 5 and in Figures 6 and 7 as 1/qe against 1/Ce.

Table 5: The values of Langmuir and Freundlich constants for adsorption of CBB dye over AC-ZnO

| Isotherms  | Parameters | Values |
|------------|------------|--------|
| Langmuir   | Qₘ         | 14.7000|
|            | Kₗ         | 0.0180 |
|            | R²         | 0.8411 |
| Freundlich | Kₕ         | 5.0750 |
|            | N          | 0.5940 |
|            | R²         | 0.8460 |

Fig. 6. Langmuir adsorption isotherm for adsorption of CBB dye over AC-ZnO

Fig. 7. Freundlich adsorption isotherm for adsorption of CBB dye over AC-ZnO

From the obtained results in above, and according to the value correlation coefficients, the value of R² for Freundlich (0.8460) isotherm is more than that for Langmuir model (0.8411). This means that
adsorption in this case is more fitted with Freundlich isotherm. According to the value of \( n \), it can be seen that its value is less than unity (0.5940) which means that adsorption in this case is fitted with the model of monolayer adsorption which means that is followed Langmuir adsorption.

**Kinetics of adsorption of CBB dye over AC/ZnO composite:** Kinetics of adsorption of CBB dye over AC-ZnO was investigated using pseudo-first order model and pseudo-second order kinetics model. The pseudo-first order model can be investigated using Lagergren and Svenska equation as follows

\[
\ln (q_t - q_e) = \ln (q_e) - k_1 t
\]

Lagren and Svenska equation

Whereas: \( q_e \) and \( q_t \) (mg/g) are the amounts of CBB dye molecules that are adsorbed at equilibrium and at a given time \( t \) (min) respectively, and the adsorption rate constant is \( k_1 \) (min\(^{-1}\)).

The pseudo-second order equation based on equilibrium adsorption can be presented following equation

\[
t/q_t = t/k_2q_e^2 + t/q_e
\]

Whereas: \( k_2 \) is the rate constant of the second order equation (g/mg min). The obtained results are presented in Table 6 and Figure 8 and 9.

**Table 6:** The values of kinetics for adsorption of CBB dye over AC-ZnO applying pseudo first order, and pseudo second order kinetics model.

| Wt (g) | Pseudo first order model | Pseudo second order model |
|-------|--------------------------|--------------------------|
|       | \( q_{e,exp} \) (mg/g)  | \( q_{e,cal} \) (mg/g) | \( k_1 \) (min\(^{-1}\)) | \( R^2 \) | \( q_{e,exp} \) (mg/g) | \( q_{e,cal} \) (mg/g) | \( k_2 \) (g/mg min) | \( R^2 \) |
| 0.05  | 28.620                   | 14.29                    | 0.128                        | 0.930       |
| 0.10  | 14.352                   | 5.640                    | 0.117                        | 0.870       |
| 0.20  | 7.289                    | 2.490                    | 0.126                        | 0.856       |
| 0.25  | 5.880                    | 1.080                    | 0.128                        | 0.637       |
| 0.05  | 28.620                   | 30.12                    | 0.380                        | 0.9350      |
| 0.10  | 14.352                   | 14.49                    | 0.256                        | 0.9988      |
| 0.20  | 7.289                    | 7.07                     | 0.0990                       | 0.9972      |
| 0.25  | 5.880                    | 5.75                     | 0.0302                       | 0.9979      |
From the obtained results it is clear that in case of Pseudo first order kinetics model the value of $q_e(\text{cal})$ is different significantly than that for $q_e(\text{exp})$. Besides that, the value of the correlation coefficient for second order model ($0.9350-0.9979$) is greater than that for the pseudo first order ($0.6370-0.9300$). These results suggest that, adsorption of CBB dye over AC-ZnO is more fitted with the Pseudo second order kinetics model\textsuperscript{39,40}.

**CONCLUSION**

In this study a composite of zinc oxide and activated carbons was synthesized successfully. The obtained results showed that combination of AC with ZnO doesn’t affect on its crystalline structure as it was conducted from XRD patterns for each of neat ZnO and a composite of AC/ZnO. The obtained results in this study, showed that, removal of CBB dye over AC/ZnO was more efficient in comparison with each of neat ZnO and neat AC under the same adsorption conditions.
REFERENCES

1. M. Mulugeta, and B. Lelisa, Mod. Chem. Appl., 2, 4 (2014).

2. F. Al-Zahraa, A. Al-Alkateeb, and F. Hussain, Desalination., 209, 342 (2007).

3. J. Emman; J. Abbas; H. Salih. Polish J. Chem. Technol., 18(3), 1(2016).

4. H. Falah; F. Ahmed; A. Hassan; A. Wisam. E.J. Chem., 7(2), 1 (2010).

5. A. Houas, H. Lachheb, M. Ksibi, E. Elaloui and C. Guillard, J. Herrmann, Applied Catalysis B: Environmental, 31, 145 (2001).

6. E. Regulska, D. Brus and J. Karpinska, International Journal of Photoenergy, 2013, 1 (2013).

7. M. Vautier, C. Guillard and J. Herrmann, Journal of Catalysis, 46, 540 (2001).

8. M. Farbod and M. Khademalrasool, Powder Technology, 40, 6605 (2014).

9. S. Senthivelan, V. Chandraboss, B. Karthikeyan, L. Natanapatham and M. Murugavelu, Mater SciSemicond Process, 16, 23 (2013).

10. N. Guy and M. Ozacar, International Journal of Hydrogen Energy, 41, 201 (2016).

11. L. Pan, G. Shen, J. Zhang, X. Wei, L. Wang and J. Zou, Industrial & Engineering Chemistry Research, 54, 7226 (2015).

12. R. Soltani, S. Jorfi, H. Ramezani and S. Purfadakari, Ultrasonics Sonochemistry, 28, 69 (2016).

13. N. Sobana, and M. Swaminathan, Sol. Ener. Mat. Sol. C., 91, 727 (2007).

14. L. Jiang, and L. Gao, Mat. Chem. Phys., 91, 313 (2005).

15. B. Rohe, W. Veeman, and M. Tausch, Nanotechnol. 17, 277 (2006).

16. T. Cordero, C. Duchamp, J. Chovelon, C. Ferronato, and J. Matos, Appl. Catal. B: Environ., 73, 227 (2007).

17. T. Cordero, C. Duchamp, J. Chovelon, C. Ferronato and J. Matos, J. Photochem. Photobio A: Chem., 191, 122 (2007).

18. Z. Wang, Journal of Physics, 16, 829 (2004).

19. A. Halbus, A. Lafta, Z. Athab and F. Hussein, Asian Journal of Chemistry; 26, 167 (2014).

20. J. Matos, J. Laine, J.-M. Herrmann, D. Uzcategui and J. Brito, Appl. Catal., B: Environ., 70, 456 (2007).

21. A. Dada, A. Olaelekan, A. Olatunya and O. Dada, Journal of Applied Chemistry, 3(1), 38 (2012).

22. A. Lafta, A. Halbus, Z. Athab, A. Hussein, A. Qhat and F. Hussein. Asian Journal of Chemistry, 26, 119 (2014).

23. F. Hussein, A. Halbus and Z. Athab. Int. J. Chem. Science, 11(3), 1219 (2013).

24. J. Guo and A. C. Lua, Mater. Chem. Phys., 80, 114 (2003).

25. B. Rohe, W. Veeman, and M. Tausch, Nanotechnology, 17, 277 (2006).

26. M. Seery, R. George, P. Floris and S. Pillai, J. Photochem. Photobiol. A: Chem., 189, 258 (2007).

27. H. Bedi, M. Kaur, R. Sharma and P. Verma, Indian Journal of Science and Technology, 9(47), 1 (2016).

28. S. Gunalan, R. Sivaraj, and V. Rajendran, Materials Research Bulletin, 46(12), 2560(011).

29. A. Taps, P. Majewski, and F. Aldinger, J. Am. Ceram. Soc., 83(12), 2954 (2000).

30. Q. Jing and X. Liu, Chin. J. Chem. Eng., 16, 890 (2008).

31. Y. Rusheng, G. Roognbo, and Z. Jingtang, Scripta Materialia, 52, 1329 (2012).

32. A. Kamil, F. Hussein, A. Halbus, and D. Bahnemann, International Journal of Photoenergy, 2014, 2(2014).

33. R Katal, M Bae, H Rahmati, H. Esfandian, and J. Indust. Eng. Chem., 18, 295 (2012).
34. M. Rahman, S Amin and A Alam, Dhaka Uni. J. Sci., 60(2), 185(2012).
35. H. Wang, C. Xie, C., W. Zhang, S. Cai, Z. Yang, and Y. Gui, J. Hazard. Mater., 141(3), 645(2007).
36. Z. El-Bahy, A. Ismail, and R. Mohamed, Journal of Hazardous Materials, 166(1), 138(2009).
37. A. Tor, N. Anaoglu, G. Arslan and Y. Congeloglu, J. Hazard. Mater., 164, 271(2009).
38. S. Karagöz, T. Tay, S. Ucar and M. Erdem, Bioresource Technology, 99(14), 6214(2009).
39. A. Kuśmierek, and A. Świątkowski, Pol. J. Chem. Technol., 17(1), 23(2015).
40. F. Ferrero, J. Hazard. Mater., 142(1), 144(2006).