Adsorption-photocatalysis of organic dyes using empty fruit bunch activated carbon-metal oxide photocatalyst

Wei Wen Loo, Yean Ling Pang*, Kam Hueil Wong, Steven Lim and Shee Keat Mah

Department of Chemical Engineering, Lee Kong Chian Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, 43000 Selangor, Malaysia.
* pangyl@utar.edu.my

Abstract. This study reports on the adsorption-photocatalysis degradation of organic dyes by utilizing zinc oxide (ZnO) photocatalyst supported on empty fruit bunch (EFB) derived activated carbon (AC) under visible light irradiation. XRD diffraction patterns of AC/ZnO sample indicated the presence of AC and ZnO. SEM analysis illustrated that ZnO particles were spherical-shaped and agglomerated, AC exhibited porous structure while AC/ZnO had agglomerated particles along the porous structure. EDX results showed that AC/ZnO sample consists of C, O and Zn elements with minimal Si and K impurities. The optimum operating conditions for adsorption-photocatalytic degradation to achieve 100 % in 50 min were initial Congo red concentration of 10 mg/L, AC/ZnO catalyst loading of 1.25 g/L, solution pH of 3 and solution temperature of 55 °C. The determination of oxygen demand analysis (64.29 % removal) indicated that only partial Congo red was being degraded due to the generation of intermediate products which were more difficult to be oxidized compared to their parent organic dye compounds. Kinetic studies which were also carried out at different solution temperatures (35, 40, 45, 50 and 55 °C) suggested that the degradation process of Congo red followed pseudo-second order model with an estimated activation energy of 86.27 kJ/mol.

1. Introduction
The coloured wastewater generated from textile industry affects the public aesthesis of water quality, as small amount of dyes that present in water will induce the recognition of colour due to the high visibility of dyes. It has been reported that about 15 % of organic dyes were discharged into the environment during synthesis and processing of textile fabric [1]. The presence of dyes in drinking water is a health hazard as it causes eye and skin irritation, haemolytic anemia, nausea, vomiting, and abdominal pain [2, 3]. Generally, dye can be classify into two types: natural and synthetic dyes [4]. Natural dyes are extracted from animal or plant sources. Synthetic dyes are organic compounds that synthesized artificially such as basic dyes, acid dyes, direct dyes and mordant dyes. It is estimated that approximately 10,000 different types of textile dyes with an annual production rate of over 7 × 10^3 metric tonnes [5, 6]. Azo dyes are the largest group (about 60–70%) of widely used synthetic dyes.

Dye removal techniques can be categorized into three methods: physical, chemical and biological method [3]. Most of the common removal techniques such as biodegradation, adsorption and flocculation are effective but time consuming and not favorable due to the high operational costs and sludge accumulation [1]. For instance, biological methods are known to be the most economical option to remove dye as compared to physical and chemical techniques. Despite of that, biological methods are restricted by cause of technical constraints such as the removal of azo dye that was not effective.
Moreover, it generates toxic aromatic amine (a human carcinogen) under anaerobic conditions [7]. Thus, photocatalytic systems based on semiconductors have been widely utilized for the degradation of organic pollutants due to the advantages of low operating costs, the possibility of eliminating complex compounds, no additional chemicals and the ability to be conducted at ambient temperature and pressure [8]. Zinc oxide (ZnO) is one of the most promising photocatalyst showing desirable properties such as high catalytic activity, low toxicity, low cost, ease in preparation, high chemical, thermal and mechanical stability [9]. Concerning the extensive research conducted by using photocatalytic degradation process in the presence of zinc oxide (ZnO) as catalyst under ultraviolet (UV) light as primary light source, the results for dye degradation were not satisfying due to the low surface area and high band gap energy of 3.37 eV. From the literature, it was found that activated carbon with large surface area, high microporous structure and energy band gap in the range (3.0–3.6 eV) is effectively for the removal of textile effluents [10]. Hence, activated carbon (AC) which has high surface to volume ratio is beneficial for adsorption followed by photocatalytic process. In spite of that, limited study focuses on the use of biomass such as agricultural wastes to derive the activated carbon. In furtherance of new idea and different statistics, this research was carried out to degrade the organic dyes by using photocatalysis method and empty fruit bunch was being utilized as the source of activated carbon to couple with ZnO as photocatalyst.

2. Experimental

2.1. Materials

Congo red (40%), methyl orange (85%), sodium hydroxide (NaOH, 97%) and zinc oxide (ZnO) were obtained from R & M Chemicals. Hydrochloric acid (HCl, 37%), potassium hydroxide (KOH, 85%) and n-Hexane were obtained from Merck while zinc nitrate (Zn(NO₃)₂, 98%), reactive blue (35%) and rhodamine B (95%) were obtained from Sigma-Aldrich. All the chemical reagents were used as received. Distilled water was used throughout the study.

2.2. Photocatalytic degradation of congo red and analysis of liquid samples

Typically, 1.0 g/L of AC-ZnO photocatalyst was put into 100 mL of 10 mg/L congo red aqueous solution in a beaker. The solution was stirred using magnetic stirrer throughout the experiment to ensure good adsorption between congo red molecules and the photocatalyst surface. Liquid samples were withdrawn at certain time intervals. The dye solution was separated from the photocatalyst using syringe filter 0.45 µm and the residual concentration of congo red was determined using a UV–vis spectrophotometer (Jenway 6320D). The measurement of maximum absorbance was performed at 498 nm. Chemical oxygen demand (COD) determination was also conducted using a Colorimetric Determination Method 80000 (DRB 200).

3. Results and discussion

3.1. SEM-EDX analyses of AC, ZnO and AC-ZnO

The surface morphology of three photocatalysts, ZnO, AC and AC-ZnO were studied using SEM analysis as shown in figure 1 (a), (b) and (c), respectively. SEM image of ZnO shows pure ZnO particles in spherical shape and agglomerated. Meanwhile, the morphology of AC exhibited fibre-like and porous in nature with plenty of grain boundaries. The pores were indicating the available of catalytic sites for adsorption and photodegradation to take place. Whilst, for AC-ZnO, the particles were randomly agglomerated around the surface of AC. The incorporation of ZnO in the carbon matrix partially blocked the porosity of the AC surface. Yang, Liao and Mao [11] reported that ZnO did not enter the inner microporosity of the AC during incorporation process but remained on the outer surface.
EDX analyses of ZnO, AC and AC-ZnO photocatalysts showed that ZnO consisted of only two peaks, which were Zn (66.56 at %) and O (33.44 at %). This indicating that there were no additional impurities and it was pure ZnO. However, C (64.29 at %), O (34.68 at %) and K (1.03 at %) were discovered in EDX spectrum of AC sample. The appearance of K peak might due to the remaining from KOH which was utilized to activate the carbon atoms. Despite of that, AC sample comprises mainly of carbon and oxygen which confirmed the chemical composition of activated carbon. Similar result was observed for AC-ZnO spectrum where there was occurrence of other slight peaks. The appearance of minority peak such as Si (2.49 at %) and K (3.07 at %) apart from the main peaks of C (45.30 at %), O (39.31 at %) and Zn (9.82 at %) found in this study. The high percentage of C, O and Zn implied that ZnO was successfully incorporated into AC. The existence of slight Si elemental peak might due to the contaminants on EDX machine sample’s plate.

3.2. XRD study
The crystalline structure of ZnO, AC and AC-ZnO photocatalysts were analysed by XRD. The results were presented in figure 2 (a), (b) and (c), respectively. The diffraction peaks of ZnO occurred at 2θ = 31.63 °, 34.29 °, 36.12 °, 56.47 °, 62.73 ° and 67.82 ° with the highest peak occurred at 36.12 °. This indicated that there was no impurity appeared in ZnO as well as other phases of ZnO, suggesting the high purity of ZnO photocatalyst [2]. The XRD pattern of AC-ZnO consists of more peaks as compared to ZnO and AC with 2θ = 21.51 °, 23.46 °, 24.72 °, 25.70 °, 32.67 °, 33.56 °, 35.60 ° and 59.02 °. There were two stronger peaks formed at 23.46 ° and 32.67 ° where the peak at 23.46 ° indicated the presence of AC while the peak at 32.67 ° represented the presence of ZnO. This clearly due to the incorporation of ZnO onto the surface of AC. Meanwhile, the diffraction peak of AC occurred at 2θ = 12.05 °, 23.98 °, 24.21 °, 30.08 °, 31.27 °, 31.78 °, 34.10 °, 37.85 °, 39.22 ° and 44.46 °. The overall XRD pattern of AC were weak. The formation of sharper peaks at 24.21 ° and 30.08 ° can be explained by the accumulation of impurities from the preparation of AC such as potassium which complied with the results from SEM-EDX. The crystallite sizes of ZnO, AC and AC-ZnO photocatalysts were calculated by using Scherrer’s equation. The calculated crystallite size for ZnO and AC photocatalysts were 41.75 nm and 43.06 nm, respectively. The smaller crystallite size of AC-ZnO, 8.02 nm could be explained the observation of broad and weak peak obtained in XRD patterns.
3.3. FTIR study

The functional groups that appeared in ZnO, AC and AC-ZnO photocatalyst were identified using FTIR analysis. Figure 3 illustrates the FTIR spectra of these catalysts in the frequency range of 600 – 4000 cm\(^{-1}\). There was a slight peak intensity for both ZnO and AC-ZnO in the range of 500 – 600 cm\(^{-1}\). This corresponded to the Zn-O stretching modes and were indicative of the formation of ZnO [3]. AC showed an intense peak at 700 – 900 cm\(^{-1}\) indicated the bending of C=O-C [2]. A sharp peak was formed for AC and AC-ZnO samples within the range of 950 -1050 cm\(^{-1}\) which was due to C-H bending vibrations [12]. Stretching vibration of aromatic ring C=C appeared within the range of 1050 – 1300 cm\(^{-1}\) by the reason of incomplete carbonisation of carbon material [13]. The sharp, intense peak for AC in the range of 1300 – 1500 cm\(^{-1}\) was due to the O-C=O stretching mode. The peak spotted at around 1600 cm\(^{-1}\) was assigned to the stretching mode of C=O in the oxalate [3, 12]. For the band of AC appeared at around 1800 cm\(^{-1}\) might be attributed to symmetric and asymmetric stretching vibrations of CH\(_2\) bonds [12]. A broad absorption peak appeared at 3300 – 3600 cm\(^{-1}\) was assigned to O-H stretching vibrations [12].

3.4. Effect of parameter studies

Figure 4 (a) shows the effect of various congo red concentration (10, 20, 30, 40 and 50 mg/L) on photocatalytic degradation of congo red at different time intervals. The results showed that the degradation efficiency decreased with the increased of congo red concentration. It was observed that the degradation efficiency decreased from 88.44% to 1.97% which was almost negligible when the congo red concentration increased from 10 to 50 mg/L. This phenomenon can be explained by the additional of the dye molecules which cause competing effect on the adsorption and reaction of O\(_2\) or OH\(^{-}\) as the
source of reactive radicals [5]. In other words, the number of reactants increased with the increase of dye molecules while the available active site of catalyst remains unchanged causing insufficient site for adsorption and photocatalytic reaction of dye molecules [14]. Apart from that, it can also be explained by the path length of photon that entered to the dye solution was decreased due to the large amount of dye molecules. This indicating more light source will be absorbed by the dye molecules instead of the catalyst [2].

Figure 4 (b) depicts the effect of various solution pH (pH 3, 5, 7, 9 and 11) on photocatalytic degradation of congo red at different time intervals. Results show that lower solution pH influenced the degradation efficiency positively. The degradation efficiency increased from 77.30% to 97.75% when the solution pH decreased from pH 11 to pH 3. This phenomenon can be explained by the structure of congo red molecules that contained sulfonic groups which can be ionized easily in acidic medium. Therefore, congo red became soluble anion and prone to be adsorbed and reacted on the positive surface charge of AC-ZnO photocatalyst. Apart from the reason stated above, congo red anions can be directly oxidized by oxygen radicals under light radiation and resulted in the high degradation efficiency. On the other hand, the decrease in degradation efficiency in alkaline solution could be explained by the basis of amphoteric behaviours of AC-ZnO photocatalyst. The surface of AC-ZnO became negatively charged when there was high concentration of hydroxide ions, causing electrostatic repulsion between dye molecules and catalyst led to the decreased in adsorption and reaction process [12]. Whereas, congo red behave as an anionic dye, which is negatively-charged. This enabled the dye molecules easier to be adsorbed and react on the positive AC-ZnO surface by electrostatic interaction [14].

Figure 4. Effect of (a) initial Congo red concentration (b) AC-ZnO photocatalyst concentration (c) solution pH (d) solution temperature (e) various types of organic dyes on photocatalysis degradation using AC-ZnO photocatalyst.

Figure 4 (c) depicts the effect of various AC-ZnO concentration (0.25, 0.50, 0.75, 1.00 and 1.25 g/L) on photocatalytic degradation of congo red at different time intervals. Results showed that the degradation of congo red was positively influenced by the AC-ZnO photocatalyst concentration where the degradation efficiency increased with increased in the concentration of AC-ZnO photocatalyst. It was found that the degradation efficiency of congo red increased from 18.48% to 94.02% when the concentration of AC-ZnO increased from 0.25 to 1.25 g/L. The reason of this observation was due to
the fact that the increased in AC-ZnO amount will directly increase the surface area and availability of adsorption site for the dye adsorption followed by degradation to occur. This phenomenon can also be explained by the degradation of congo red was favoured by increasing AC-ZnO loading as increased in active sites led to the enhancement of production and reaction of -OH radicals [2]. These observation trend is similar to those reported in literature for the adsorption of Rhodamine B by mesoporous carbon material [12].

The effect of solution temperature (35, 40, 45, 50 and 55 °C) on the photocatalytic degradation of congo red was experimented and shown in figure 4 (d). It showed a positive impact when the solution temperature was raising from 35 °C to 55 °C, degradation efficiency increased from 92.88% to 100%. The significant degradation efficiency was clearly observed in the first 10 min, which averagely got a result as high as 90% degradation. It was worth being noted that a 100% of degradation efficiency was achieved at the end of the experiment when the temperature was set to 55 °C. The increased in degradation efficiency of congo red with rising in solution temperature was owing to the fact that higher solution temperature increased the activation energy of reaction and therefore, more collision occurred between molecules caused the increased in reaction rate. The mass transfer between photocatalyst molecules and dye molecules increased at the same time [6]. Furthermore, this phenomenon might be attributed to the increased diffusion of dye molecules towards the external boundary layer of catalyst. Elevated solution temperature enhanced the diffusion of dye molecules into the pores of photocatalyst [12].

The effect of several types of organic dyes such as Congo Red, Methyl Orange, Methylene Blue, Reactive Blue and Rhodamine B for adsorption and photodegradation processes were investigated by utilizing three types of photocatalysts included ZnO, AC and AC-ZnO. Based on the observation as indicated in figure 4 (e), methylene blue clearly possesses the best degradation efficiency under all three types of catalyst, while reactive blue recorded the lowest degradation efficiency among all types of organic dyes. As for methylene blue, high degradation efficiency was due to its nature as a cationic dye where electrostatic attraction can occur easily between dyes and Ac-ZnO and reacted with photo-generated electrons [15]. Besides, the contribution of adsorption of AC and AC-ZnO on methylene blue were found as high as 76.81 % and 79.58 %, indicated photocatalytic reaction did not contribute much for the degradation efficiency. Rhodamine B is a xanthene dye, which was harder to be degraded due to its superior light resistance as well as ultrahigh solubility in water [16]. Meanwhile, low degradation efficiency of reactive blue might be attributed to the presence of anionic sulfonate groups which lower the chances of adsorption of reactive blue to take place [1]. It was found that adsorption of congo red by ZnO achieved 18.16 %, AC recorded 9.69 % while AC-ZnO achieved 27.39 %. Congo red and methyl orange were anionic dye. A negatively-charged chromophore was produced when ionized in water. This allowed them to be able to adsorb easier by the positive charge photocatalyst surface and thus, recorded better degradation efficiency. AC-ZnO photocatalyst achieved the highest catalytic activity was mainly due to the availability of large amount adsorption sites for reaction as compared to the other two photocatalysts. In addition, the degradation efficiency was influenced by the structures of organic dyes itself [17]. From the results shown, congo red, methyl orange and methylene blue had relatively higher degradation efficiency which was above 80%. Photocatalysis process was preceded by the adsorption of substrate molecules on the surface of catalyst to ensure the effective contact with electrons or holes to occur.

COD analysis was conducted and it was found that 54.76% of COD had been removed after 30 min while 64.29 % of the COD had been removed after 50 min of reaction. The partial removal of COD might be due to various intermediates products that produced during the photodegradation of congo red. These intermediate products that were hard to be oxidized as compared to parent compounds. It can also be explained by the nature of congo red where asymmetric oxidative cleavage led to the formation of mono azo intermediates initially which can be further oxidatively and reductively cleaved into simple metabolites. Thus, it was anticipated that higher percentage of COD removal could only be achieved by proceeding the experiment for a longer period.
3.5. Possible mechanism

The mechanism on AC-ZnO to degrade dye molecules is illustrated in figure 5. When UV light source strikes on the surface of AC-ZnO, the electrons are excited from valence band (VB) into conduction band (CB), leaving the holes behind [14]. The electrons (e\(^{-}\)) and holes (h\(^{+}\)) pairs were available for oxidation and reduction to take place and then lead to the formation of ·OH radicals, which was the most crucial radicals for the photocatalytic degradation to occur. Besides, the oxygen molecules adsorbed on ZnO then formed superoxide anion radicals, ·O\(_{2}\) because of their interaction with electrons in the conduction band of ZnO. Meanwhile, the hydroxyl groups on surface produce highly reactive hydroxyl radicals, ·OH by reacting with the holes in the VB of ZnO. The dye molecules are finally degraded by the reaction with both ·O\(_{2}\) and ·OH radicals [15]. The presence of AC can enhance the adsorption capacity of Congo red and improve the separation efficiency of electrons and holes [11]. In other words, AC-ZnO was an effective photocatalyst for photocatalysis process. The reactions that take place are indicated by equations (1) – (5).

\[
\begin{align*}
\text{ZnO + light source} & \rightarrow \text{h}^{+} + \text{e}^{-} \\
\text{h}^{+} + \text{H}_2\text{O} & \rightarrow \text{OH}^{-} + \text{h}^{+} \\
\text{h}^{+} + \text{Dye} & \rightarrow \text{oxidation products} \\
\text{e}^{-} + \text{Dye} & \rightarrow \text{reduction products} \\
\text{OH}^{-} + \text{Dye} & \rightarrow \text{degradation products}
\end{align*}
\]

**Figure 5.** Schematic diagram of photodegradation mechanism of dye molecules.

3.6. Kinetic Study

Kinetic studies were performed on the basis of the rate of disappearance of congo red in order to determine the order of the reaction for photocatalytic degradation of the dye. In figure 6 (a), the plot of \(1/C_t vs t\) shows a linear relationship, from which rate constant, \(k_{\text{app}}\) can be determined from the slope of the plot. This indicated that the adsorption and reaction of congo red at different solution temperatures was recorded as pseudo second-order kinetics. Therefore, the slope of the straight lines should be equal to the apparent second-order rate constant (\(k_{\text{app}}\)). It was also observed that the pseudo second-order rate constant increased with increasing solution temperature where the \(k_{\text{app}}\) increased from 0.0887 to 0.3251 L/mg·min when the solution temperature increased from 35 °C to 50 °C. This was due to the accelerated production of OH radicals when the solution temperature increased and therefore, contributed to the gradual increase of rate constant [6].

Based on figure 6 (b), the plot was a considerably good linear graph with \(R^2\) value of 0.9695. The Arrhenius relationship can be implied by equation (6).

\[
\ln k_{\text{app}} = -10381 \left( \frac{1}{T} \right) + 31.149, \quad R^2 = 0.9695
\]
From equation (6), $E_a$ and $A_0$ can be determined by the slope ($E_a/R$) and intercepts ($\ln A_0$) of the linear plot, respectively. $E_a$ and $A_0$ for degradation of congo red was 86.27 kJ/mol and $3.37 \times 10^{13}$ L/mg-min, respectively. Tekin and Derya [18] reported that the $E_a$ for photodegradation of congo red was 56.1 kJ/mol. Their result showed lower $E_a$ value as compared to the photocatalytic degradation of congo red in current study, which was 86.27 kJ/mol. This implied that higher solution temperature was required to overcome the $E_a$. Higher $E_a$ value indicated that the reaction was mainly influenced by solution temperature as compared to the concentration and life of reactive free radicals.

![Figure 6](image_url)

**Figure 6.** (a) Pseudo second-order reaction kinetics plot for photocatalytic degradation of congo red (b) Arrhenius plot of $k_{app}$ against $1/T$.

### 4. Conclusions

ZnO, AC and AC-ZnO photocatalyst were successfully synthesised and characterised. AC was prepared by calcination in a furnace at temperature of 450 °C for 2 hrs while ZnO was synthesised by using zinc precursor. These three types of photocatalysts were then characterised by XRD, SEM-EDX and FTIR analyses. XRD diffraction patterns of AC-ZnO sample indicated the presence of AC and ZnO. SEM results showed that ZnO particles were in spherical shape and agglomerated, AC exhibited porous structure while AC-ZnO had agglomerated particles along the porous structure. Whilst, EDX results illustrate that ZnO contained only Zn and O elements, AC contained elements of C and O together with K impurities which resulted from the preparation of AC. Meanwhile, AC-ZnO sample shows the presence of Zn, O, C, Si and K elements impurities. The optimum conditions for degradation efficiency...
of congo red were obtained at an initial dye concentration of 10 mg/L, initial dosage of AC-ZnO photocatalyst at 1.25 g/L, solution pH of 3 and solution temperature of 55 °C for 50 min to achieve 100% degradation efficiency. However, only partial COD (64.29%) was being removed. This was due to the generation of intermediate products which were more difficult to be oxidized as compared to parent organic dye compounds. On the other hand, the reaction kinetics of photocatalytic degradation of congo red at different solution temperature (35, 40, 45, 50 and 55 °C) were followed pseudo second-order kinetics. The $E_a$ and $A_o$ for photocatalytic degradation of congo red were 86.27 kJ/mol and $3.37 \times 10^{13}$ L/mg·min, respectively.

Acknowledgments

This study was financially supported by Universiti Tunku Abdul Rahman Research Grant through the Centre for Photonics and Advanced Materials Research and Centre for Environment and Green Technology (CEGT), UTAR (IPSR/RMC/UTARRF/2018-C1/P01). The financial support provided by Fundamental Research Grant Scheme by the Ministry of Education (MOE) Malaysia is also gratefully acknowledged.

References

[1] Kakarndee S and Nanan S 2018 *J. Environ. Chem. Eng.* 6 74-94
[2] Ong C B, Mohammad A W, Rohani R, Ba-Abbad M M and Hairom N H H 2016 *Process Saf. Environ. Prot.* 104 549-557
[3] Intarasuwan K, Amornpitoksuk P, Suwanboon S and Graided P 2017 *Sep. Purif. Technol.* 177 304-312
[4] Lipskikh O I, Korotkova E I, Khristunova Y P, Barek J and Kratochvil B 2018 *Electrochim. Acta* 260 974-985
[5] Yang C, Yu J, Li Q and Yu Y 2017 *Mater. Res. Bull.* 87 72-83
[6] Zangeneh H, Zinatizadeh A A L, Habibi M, Akia M and Hasnain Isa M 2015 *J. Ind. Eng. Chem.* 26 1-36
[7] Ma C, Wang F, Zhang C, Yu Z, Wei J, Yang Z, Li Y, Li Z, Zhu M, Shen L and Zeng G 2017 *Chemosphere* 168 80-90
[8] Mohamed A, El-Sayed R, Osman T A, Toprak M S, Muhammed M and Uheida A 2016 *Environ. Res.* 145 18-25
[9] Qi K, Cheng B, Yu J and Ho W 2017 *J. Alloys Compd.* 727 792-820
[10] Soliman A M, Elsucary S A A, Ali I M and Ayesh A I 2017 *J. Water Process Eng.* 17 245-255
[11] Yang Q, Liao Y and Mao L 2012 *Chin. J. Chem. Eng.* 20 572-576
[12] Saini J, Garg V K, Gupta R K and Kataria N 2017 *J. Environ. Chem. Eng.* 5 884-892
[13] Mo X, López D E, Suwannakarn K, Liu Y, Lotero E, Goodwin Jr J G and Lu C 2008 *J. Catal.* 254 332-338
[14] Abdelwahab N A and Helaly F M 2017 *J. Ind. Eng. Chem.* 50 162-171
[15] Wang S, Zhou Y, Han S, Wang N, Yin W, Yin X, Gao B, Wang X and Wang J 2018 *Chemosphere* 197 20-25
[16] Lin K-Y A and Lin J-T 2017 *Chemosphere* 182 54-64
[17] Rao A N S and Venkataraangaiah V T 2014 *Port. Electrochim. Acta* 32 213-231
[18] Tekin D 2014 *Prog. React. Kinet. Mech.* 39 249-261