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Combined catalytic ozonation and electroflocculation process for the removal of basic yellow 28 in wastewater

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ABSTRACT

The study aims to investigate the decolourization of basic yellow 28 by catalytic ozonation and electroflocculation using iron loaded rice husk ash (Fe-RHA) as catalyst. The comparative study of various advanced oxidation processes such as ozonation, catalytic ozonation, electro flocculation and combined process was conducted. In addition, the kinetic considerations were applied and rate constants of various processes were compared. Finally, chemical oxygen demand (COD) and decolourization efficiencies were studied. The comparison among the advanced oxidation processes at pH 7 shows that the maximum removal of 75.8% was achieved by synergetic process (electroflocculation and catalytic ozonation using Fe-RHA catalyst). Increase in catalyst dose showed enhancement in decolourization by the synergetic process, maximum decolourization of 87.3% was achieved in 120 min with 60 g Fe-RHA. The COD removal was found to be significant (52% in 120 min) in combined process. The pseudo-first-order kinetic model was applied to the processes, rate constant of synergetic process was found to be the highest that was 11.2×10^{-3} min^{-1}. Therefore, it is concluded that catalytic ozonation in combination with electroflocculation process was an effective method for the decolourization of basic yellow 28 near wastewater pH.

Keywords: Catalytic ozonation; Electroflocculation; Basic yellow 28; Rice husk ash

1. Introduction

Advanced oxidation processes (AOP) are powered by strong oxidants such as hydroxyl radicals for the destruction of recalcitrant organic pollutants in wastewater and transform them into nontoxic products [1]. AOPs involve various aqueous phase oxidation methods producing highly reactive species as hydroxyl radicals with an oxidation potential of 2.80 V for the treatment of wastewater contaminants and complete mineralization into water, carbon dioxide and inorganic ions [2]. The various AOPs techniques for the treatment of organic pollutants includes ozonation [2], catalytic ozonation [3], Fenton processes [4], electrochemical AOP [5] were implied for the degradation of organic pollutants from wastewater.

Ozonation is an efficient method for the complete degradation and mineralization of chromophoric groups of textile dyes by attacking conjugated double bonds [2]. Catalytic ozonation and single ozonation causes the degradation of organic pollutants both by direct reaction mechanism, that is, ozone attack, and indirect reaction mechanism, that is,

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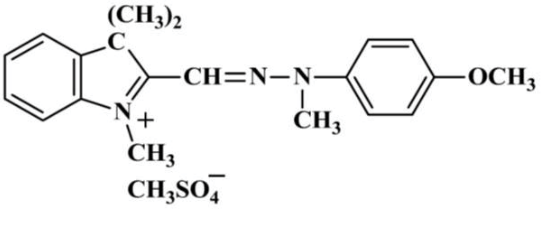
free radical mechanism, simultaneously [1,2]. The ozonation processes have certain advantages such as no sludge production, less area required, single step process and easy decomposition of residual ozone to water and oxygen [6]. The limitations of single ozonation include low stability due to short half-life, low solubility and high cost [7]. Catalytic ozonation enhances the rate and efficiency of ozone oxidation process [3,7].

Electroflocculation is an electrochemical oxidation process in which anodic oxidation causes in situ production of coagulants for the removal of organic pollutants in wastewater [8]. When the current passes through anode, made of mostly Fe or Al, metal cations are formed that react with the hydroxyl ions generated at cathode to form various gelatinous metallic hydroxide and polyhyroxide species causing pollutants adsorption and precipitation. Moreover, gases released at anode and cathode, that is, oxygen and hydrogen, initiate pollutant flotation to surface which may then removed [8].

Dyes are an important class of pollutants found in effluents of textile industries, tanneries, dye manufacturing units and pulp and paper industries [9]. Dyes are toxic and carcinogenic thereby disturbing the aquatic life when discharged into water bodies by impeding the light penetration and photosynthesis and cause mutation, skin irritation and allergic dermatitis in humans [9,10]. In this study, basic yellow 28 (BY 28) (cationic dye) was used as model textile dye. (Fig. 1)

To avoid the environmental hazards, proper colour removal treatment in wastewater is necessary. Various techniques for the treatment of dyes were tested such as ozonation [3,6], Fenton processes [4,11], adsorption [12,13], electrochemical processes [5,8], membrane filtration [14,15], ion exchange [16,17], biological process [18] and chemical coagulation and flocculation [9,19]. Various studies on ozonation coupled with electrochemical treatment have been reported to be highly efficient [20–22]. In current investigation, iron-loaded rice husk ash (Fe-RHA) was implied in catalytic ozonation process coupled with electroflocculation. To the author's knowledge, Fe-RHA was previously studied in combined catalytic ozonation and electrochemical treatment process.

Rice husk ash (RHA) is a waste product formed in biomass power plants. RHA is mainly composed of amorphous silica, carbon and minerals [23]. RHA has been widely used as an adsorbent for the removal of dyes from aqueous solution [10,12] and it has also been used as a catalyst in Fenton-like oxidation processes [11]. Moreover, iron-loaded supports were affectively used for degradation of organic pollutants [24]. Therefore, this study may help to explore an efficient and economical catalyst in electrochemical processes coupled with ozonation, used for the treatment of wastewater. Furthermore, in this study, effect of pH on degradation of BY 28 using ozonation, catalytic ozonation, electroflocculation, and integrated catalytic ozonation and electroflocculation was studied. In addition, catalyst dose effect, decolourization efficiencies were compared with chemical oxygen demand (COD) removal and kinetics considerations were implied to compare and further understand the oxidation processes.



Type: Basic Cationic Dye
pH stability: 3-10
λ_{max}: 438nm

Chemical Formula: $C_{21}H_{27}N_3O_5S$
Molecular weight: 433.52 g/mol

Fig. 1. Properties and structure of basic yellow 28.

2. Experimental

2.1. Materials and reagents

BY 28 was obtained from May & Baker, UK. The pH adjustment of solution was done using 0.1 N HCl and NaOH purchased from Merck, Germany. All solutions were prepared using ultrapure deionized water. The RH was obtained from the local market. All the chemicals used were of analytical grade and were used without further purification.

2.2. Catalyst preparation and characterization

The incipient impregnation method was used to prepare Fe-RHA catalyst [25,26]. The RH obtained from local market was washed with distilled water to remove dust and other particles. The cleaned RH was dried in air for 48 h. Then, it was placed in a furnace for 6 h at 600°C, to obtain ash. For further purification the powdered material obtained was soaked in 0.1 M nitric acid for 24 h, it was then filtered (using suction filtration assembly) and then rinsed in the deionized water two to three times until a constant pH was obtained. Finally, the material was dried overnight in an oven at 110°C [27]. The Fe-RHA catalyst was prepared by impregnating iron (III) oxide using incipient impregnation method [25,26].

The surface morphology of RHA and Fe-RHA was analysed by using scanning electron microscope (SEM), model, JSM-6010LA. Brunauer–Emmett–Teller (BET) method (micro metrics ASAP 2020) was applied to determine the surface area and pore size. The structural analysis of RHA and iron-loaded RHA were investigated by PANalytical X'Pert MPD X-ray diffractometer with Cu K-α radiations (λ = 1.5406 Å) operated at 40 kV and a current of 40 mA in (θ–θ) scan mode scanning all the specimen in the 2θ range between 20° and 80° with scan step of 0.02°. Finally, the point of zero charge of Fe^{+3}-RHA was determined by mass transfer method [28].

2.3. Experimental setup

Ozone was produced from air using ozone generator (AZCO HTU-5000GE-120) and was supplied at a rate of 0.9 mg/min. The ozonation and catalytic ozonation experiments were performed in a rectangular plexiglass reactor with the dimensions of 203 mm × 152 mm × 152 mm. Ozone entered the reactor through inlet port and left through the outlet port. Sampling port was also provided at the bottom of the reactor (Fig. 2). The ozone was introduced into the reactor through a diffuser to generate fine bubbles. The excess ozone leaving the reactor was trapped using sequential 2% KI traps (Fig. 2).

Electroflocculation experiments were performed in above-mentioned rectangular plexiglass reactor, the electric current was supplied using DC power supply with a rating of 0–5 Å and 0–40 V. The reactor consisted of two identical Al mesh electrodes having dimensions of 50 × 50 mm, installed vertically in monopolar connection with 20 mm electrode gap. The magnetic bar at the bottom of the reactor provided stirring.

Ozonation-electroflocculation combined experiments were performed in the same reactor with both setups of ozonation and electroflocculation installed simultaneously as shown in Fig. 2.

2.4. Experimental procedure

Ozonation experiments were performed by taking 3,000 mL of dye solution having concentration of 25 mg/L in the reactor. The required pH of solution was set using 1 N HCl and NaOH. The experiments were performed by supplying ozone from ozone generator at a rate of 0.9 mg/min. Samples were withdrawn at regular time intervals of time and concentration of dye was analysed by double beam UV-vis spectrophotometer (Perkin Elmer Lambda 35). The excess ozone leaving the reactor was introduced into two 2% potassium iodide traps (Fig. 2).

Catalytic ozonation experiments were performed by adding desired amount of catalyst in the reactor and using the same procedure as that of ozonation. The magnetic stirrer at a rate of 300 rpm provided stirring.

Electroflocculation experiments were performed using above-mentioned steps. The electrolyte NaCl was added to the solution at a concentration of 1 g/L to promote higher conductivity. The experiment was started by supplying current using DC power supply at a constant voltage of 30 V. Stirring was provided by the magnetic stirrer at a rate of 300 rpm. Samples were withdrawn at regular time intervals and concentration of dye was analysed by double beam UV-vis spectrophotometer (Perkin Elmer Lambda 35). After each run, the electrodes were rinsed in 0.1 N HCl and were cleaned.

Electroflocculation-Fe-RHA experiments were performed by adding desired amount of catalyst in the reactor and using the same procedure as that of electroflocculation. Ozonation-electroflocculation experiments were performed by combining the two procedures.

2.5. Analysis

2.5.1. Basic yellow 28 analysis

The BY 28 concentrations in the solution were analysed using double beam UV-vis spectrophotometer (Perkin Elmer Lambda 35). The λ_{max} was found at 438 nm by analysing the BY 28 absorbance in the visible range. The decolourization efficiency was determined by applying the following formula:

$$\text{Percentage removal}(\%) = \frac{\left(A_o - A_t\right)}{A_o} \times 100 \qquad (1)$$

where A_o = initial absorbance; A_t = final absorbance at time t.

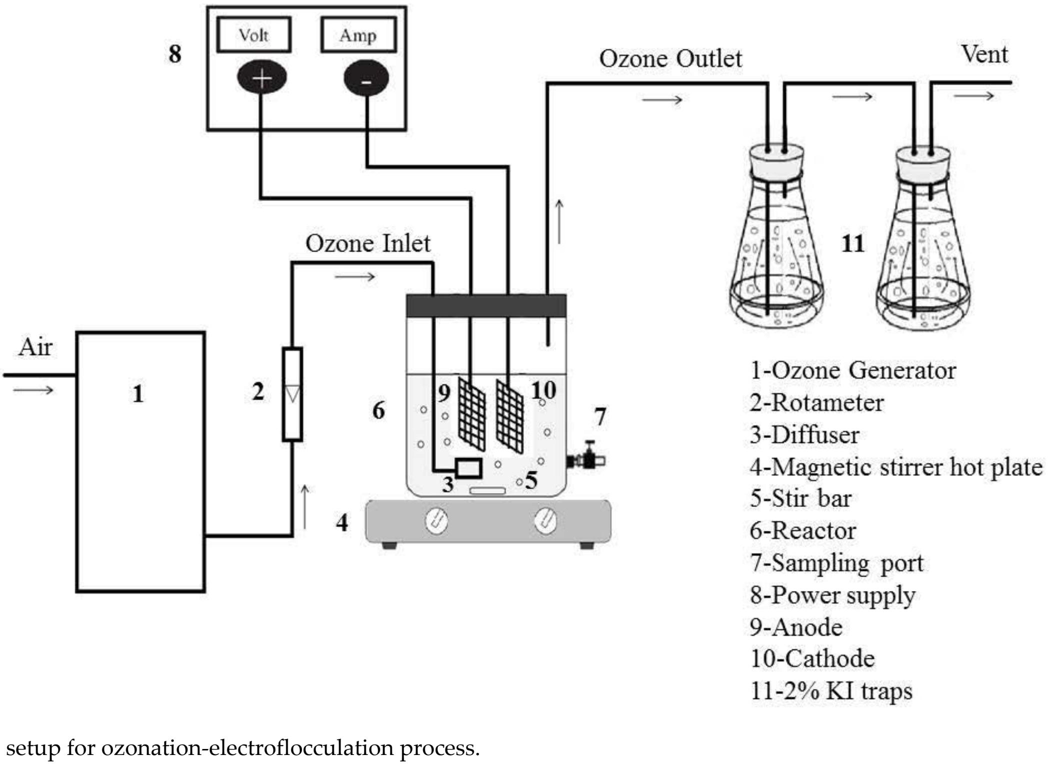


Fig. 2. Reactor setup for ozonation-electroflocculation process.

2.5.2. Ozone dose analysis

In order to quantify ozone dose, iodometric method has been used [29]. In this method, ozone generated from ozone generator (AZCO HTU-5000GE-120) was introduced into the two sets of 2% KI traps, each filled with 100 mL of the solution. Then, each set was quenched with 5 mL of 2 N H_2SO_4 to liberate iodine. The liberated iodine was then titrated against 0.005 N $Na_2S_2O_3$ using starch indicator [29]. Ozone dose was calculated by using following formula:

$$\text{Ozone dose}\left(\frac{mg}{\min}\right) = \frac{V \times N \times 24}{T} \quad (2)$$

where V, total volume of the titrant used; N, normality of $Na_2S_2O_3$; T, ozonation time.

3. Results and discussion

3.1. Catalyst characterization

The comparative results of BET surface area for RHA and Fe-RHA show that the incorporation of Fe^{3+} leads to a decrease in surface area (Table 1). The reduction in surface area by iron loading may be due to the capping of the pores by loaded iron [30]. It is important to mention here that similar trends were obtained in some previous findings [30]. Surface area was found to be 80.1, 90.5 m^2/g and the average pore size was 19.5, 18.2 Å for Fe-RHA and RHA, respectively (Table 1). As compared with previous findings, the surface area of Fe-RHA was found to be higher than reported by some findings [11] and was less than by some other reports [27]. The point of zero charge was determined by mass transfer method [28] and was slightly higher for iron-loaded RHA, this may be due to the iron loading, it was $pH_{pzc} = 3.3 \pm 0.2$ and 2.9 ± 0.1 for RHA and Fe-RHA, respectively (Table 1). The SEM images of both RHA and Fe-RHA indicate (Fig. 3) that no significant change in surface morphology was observed after the incorporation of iron on RHA. The energy dispersive X-ray (EDX) analysis clearly indicates the iron loading in the case of Fe-RHA (Fig. 4). The EDX analysis further show that mass percentage of loaded iron was 29.37% in Fe-RHA (Fig. 4).

The patterns obtained in X-ray diffraction (XRD) (Fig. 5) were found to be in agreement with the results presented in earlier reports [27]. The results show that no sharp peak was observed for Fe-RHA. It indicates a good dispersion of microcrystalline iron particles on the silica support. Moreover, the slightly broader peaks appeared in the case of Fe-RHA may be due to the possible slight shift in structural changes from amorphous to crystalline, however, this may be difficult to detect due to the microcrystalline nature of particles [30].

Table 1
Characteristics of Fe-RHA catalyst

Material	Surface area (m^2/g)	Average pore size (Å)	pH_{pzc}
Fe-RHA	80.1	19.5	3.3 ± 0.2
RHA	90.5	18.2	2.9 ± 0.1

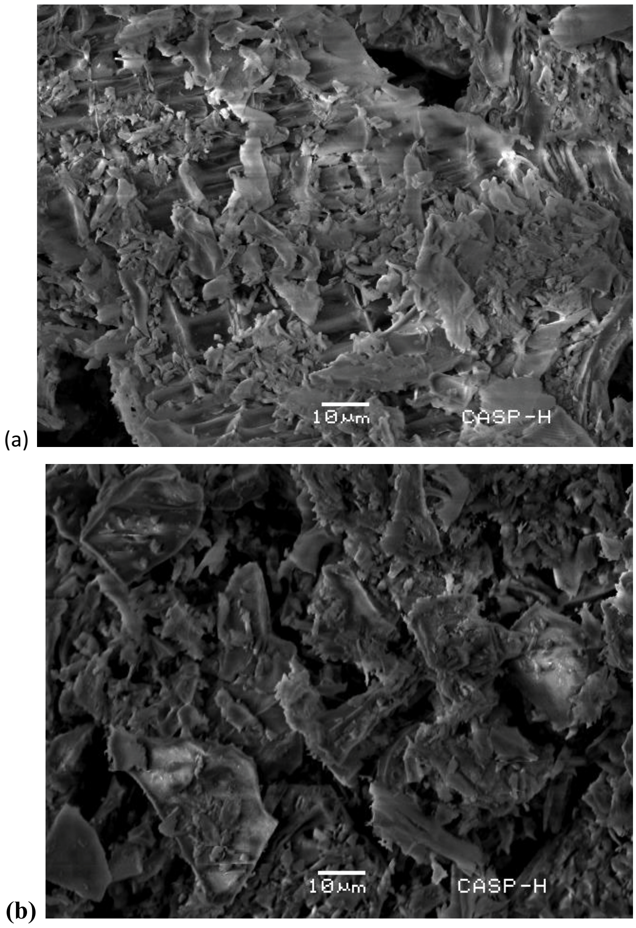
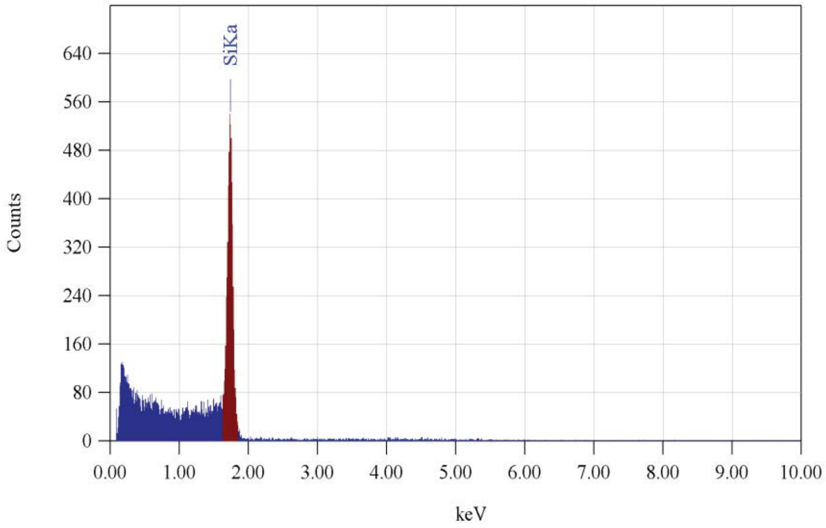


Fig. 3. SEM images of (a) Fe-RHA and (b) RHA.

3.2. Effect of pH on decolourization

The initial pH of the solution effects the dye removal significantly. Therefore, BY 28 decolourization was studied at three different pH values (acidic, pH 3; neutral, pH 7 and basic, pH 10). Fig. 6 revealed that the Fe-RHA catalytic ozonation caused more effective decolourization as compared with ozonation and electroflocculation. With an increase in pH, dye removal increased for both catalytic ozonation and ozonation. For example, under acidic conditions (pH 3), the percentage decolourization efficiencies in catalytic ozonation, ozonation and electroflocculation were 54.10%, 41.40% and 27.90%, respectively, at time 120 min (Figs. 6(a)–(c)). In the case of single ozonation, in acidic conditions, ozone may directly attack the dye via slow reaction [7]. Moreover, ozone cause degradation of dye by splitting the unsaturated bonds in the dye structure [31]. In case of catalytic ozonation process, the surface of iron-loaded RHA may be neutral near its point of zero charge, therefore, ozone may interact with Bronsted acid sites and hence results in the production of hydroxyl radicals [24]. Therefore, higher removal efficiency of BY 28 was achieved in the case of catalytic ozonation process (at pH 3) as compared with single ozonation (Fig. 6(a)). The chemical species generated in the aqueous solution by electroflocculation may primarily dependent on pH. At acidic pH 3, the efficiency of electroflocculation was found to



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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.3592
Element         (keV)   mass%  Error%     At%  Compound    mass%  Cation          K
Si K            1.739  100.00    0.45  100.00                             207.3167
Total                  100.00          100.00
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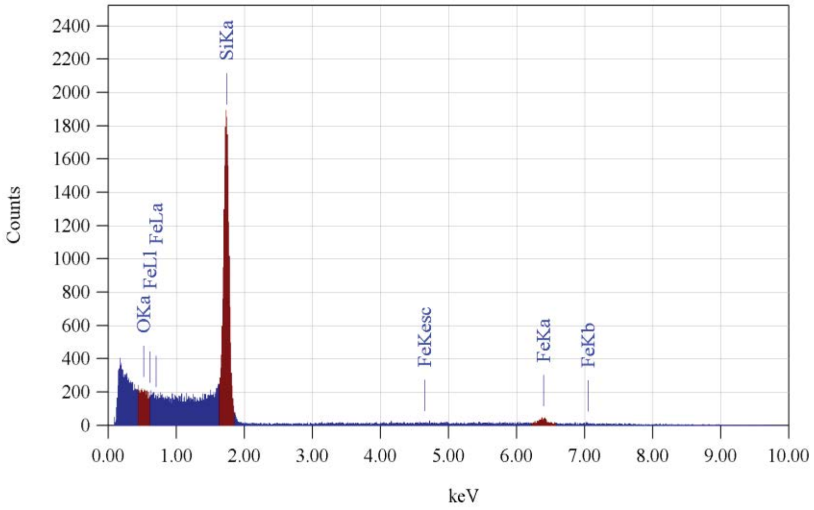
(a)



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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.3054
Element         (keV)   mass%  Error%     At%  Compound    mass%  Cation          K
 O K*           0.525    0.63    0.23    1.28                               1.4229
Si K            1.739   70.01    0.29   81.52                             178.0380
Fe K            6.398   29.37    4.86   17.20                              65.4333
Total                  100.00          100.00
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(b)

Fig. 4. EDX of (a) RHA and (b) Fe-RHA.

be lower (Fig. 6(a)). This may be because aluminium exists in the form of free cations Al^{3+} [20].

The results further reveal that the dye removal efficiency increases with the increase in pH, at neutral pH conditions (pH 7), the decolourization efficiencies achieved were 69.40%, 56.10%, 40.80% in catalytic ozonation, ozonation and electroflocculation, respectively, at time 120 min (Fig. 6(b)). The electroflocculation process shows better removal efficiency (at pH 7) as compared with pH 3, this may be because the formation of gelatinous aluminium hydroxide complexes, $Al(OH)_3$ complexes may be the predominant species which causes dye removal by adsorption. Freshly formed amorphous $Al(OH)_{3(s)}$ 'sweep flocs' have large surface areas, which may be beneficial for a rapid adsorption of soluble organic compounds [20]. The ozonation in the presence of catalyst effectively attacked and removed the BY 28. The presence of Fe-RHA during the ozonation of BY 28 causes the increase in ozone dissolution by providing the surface [7]. At higher pH

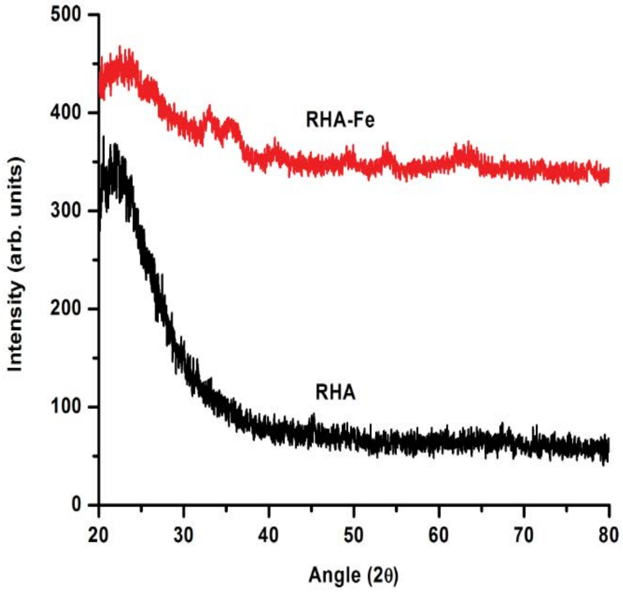


Fig. 5. XRD patterns of Fe-RHA and RHA.

values above the point of zero charge of catalyst (pH_{pzc} = 3.3), that is, neutral and alkaline conditions, the catalyst Fe-RHA surface becomes negatively charged [24] and degree of protonation of Fe-RHA surface decreases gradually thereby increasing the adsorption of the cationic dye onto the catalyst surface [32]. The adsorbed dye on the catalyst surface may be removed by adsorbed hydroxyl radicals formed inside the solution.

At pH 9, $Al(OH)^{4-}$ form may be the dominant specie that could remove the dye by electrostatic interaction and precipitation [20]. Under alkaline conditions (pH 9), the decolourization efficiencies achieved were 64.10%, 61.60%, 34% in catalytic ozonation, ozonation and electroflocculation, respectively, at time 120 min. Under alkaline conditions, ozone decomposition generates hydroxyl radicals, which have high oxidation potential, and causes fast degradation of dye.

3.3. Comparison among advanced oxidation processes:

The comparative study among the AOP or synergetic processes such as Fe-RHA catalytic ozonation, ozonation-electroflocculation, electroflocculation aided by Fe-RHA and

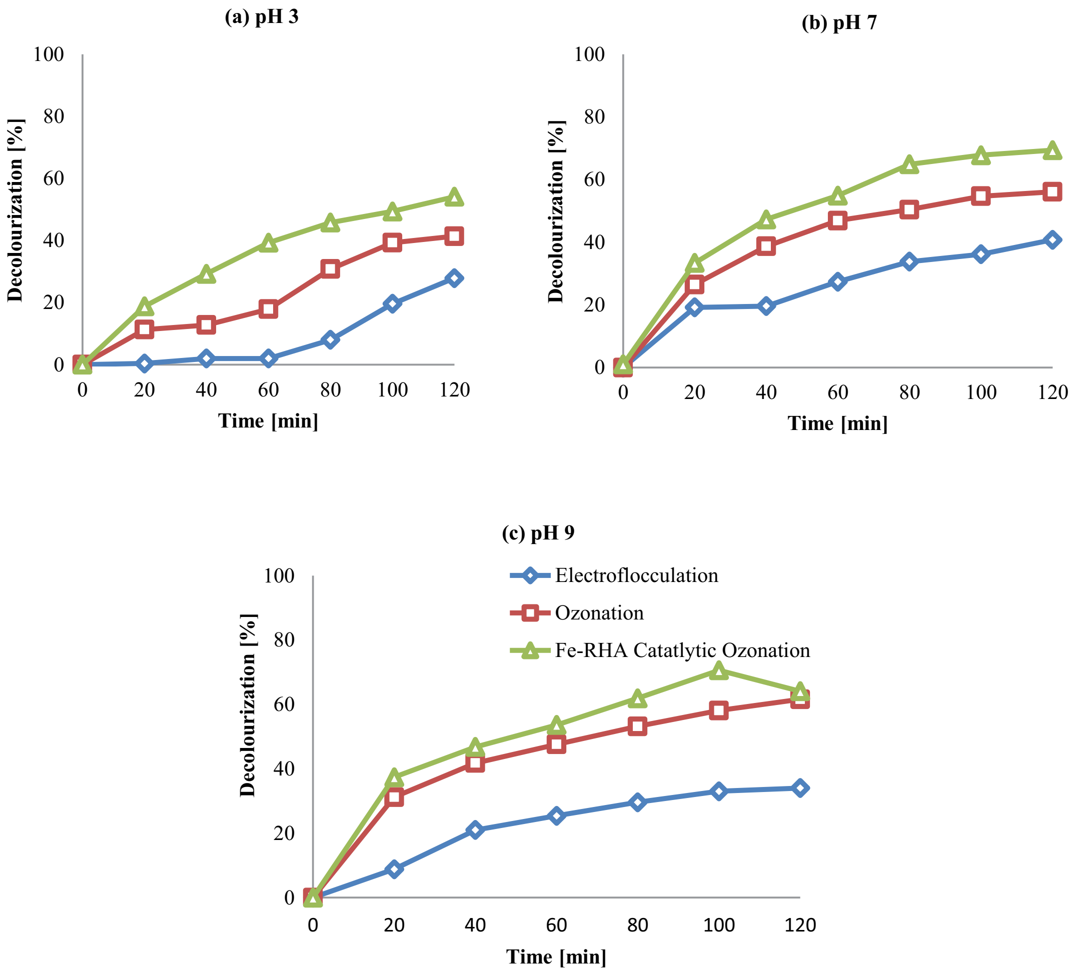


Fig. 6. Effect of pH on the decolourization of basic yellow 28 in the electroflocculation, ozonation and Fe-RHA catalytic ozonation processes (Co (BY) = 25 mg/L; T = 30°C; catalyst amount = 40 g; V = 3,000 mL; O_3 = 0.9 mg/min; voltage = 30 *V*; current = 0.34 Amp).

Fe-RHA catalytic ozonation-electroflocculation was studied at neutral pH 7 (Fig. 7). The maximum dye removal efficiency of 75.80% was obtained in the case of Fe-RHA catalytic ozonation-electroflocculation synergetic process in 120 min. This may be explained, as the performance of electroflocculation is high at neutral pH due to the maximum formation of aluminium poly hydroxide species that causes the dye removal by charge neutralization and adsorption. The Fe-RHA catalytic ozonation is also very effective process at pH 7, as the catalyst surface becomes negatively charged, hence BY 28 adsorption may increase and hydroxyl radicals formed inside solution may adsorbed on catalyst surface to remove adsorbed dye. It is important to mentioned here that synergic process has about 10% higher removal efficiency as compared with catalytic ozonation process at pH 7 (Fig. 7). This may be due to the change in surface properties of iron-loaded catalyst at pH higher than its point of zero charge (the surface hydroxyl groups may be deprotonated [24]) and the removal of dye was mainly due to the adsorption mechanism in both processes [24,30,33].

3.4. Effect of Fe-RHA dose

The effect of catalyst dose on the Fe-RHA catalytic ozonation electroflocculation synergetic process for the treatment of BY 28 was studied at 20, 40 and 60 g dosage. The percentage decolourization increased with the increase in catalyst dose (Fig. 7). The maximum decolourization of 87.3% was achieved (at 60 g dosage, in 120 min). The increase in dye removal with the catalyst dose may be due increase in adsorption [34], which clearly indicates that catalyst plays an important role in combined process.

3.5. Decolourization versus degradation

The results presented in Fig. 9 clearly indicate that the decolourization of BY 28 was much higher as compared with its degradation. For example, 75.8% decolourization efficiency was achieved in first 120 min. However, the efficiency in terms of COD removal was found to be 52.2% in 120 min (Fig. 9). The experimental data indicate that combined process (catalytic ozonation-electroflocculation) found to be highly effective to remove COD near wastewater pH.

3.6. Kinetic studies

The pseudo-first-order kinetic models were applied to decolourization of BY 28 [35].

$$-\frac{dC}{dt} = kC \tag{3}$$

In linearized form,

$$\ln\left(\frac{C_o}{C_t}\right) = kt \tag{4}$$

where C_o = initial dye concentration (mg/L); C_t = concentration at time t (mg/L); t = time (min); k = the pseudo-first-order rate constant (min^{-1}).

The linear plots of pseudo-first-order kinetic model as shown in Fig. 10 showed that model fitted well to the decolourization of BY 28 with studied processes. The values of the rate constants and regression coefficients have been given in Table 2. It was observed that highest value of rate constant of 11.2 × 10^{-3} min^{-1} was achieved for the synergic process (electroflocculation and catalytic ozonation using Fe-RHA catalyst).

3.7. Proposed mechanism of synergic process

The integrated process studied in current investigation involves the combined effect of two different processes for the removal of BY 28. The mechanism of both the electroflocculation and catalytic ozonation processes depends on the pH of

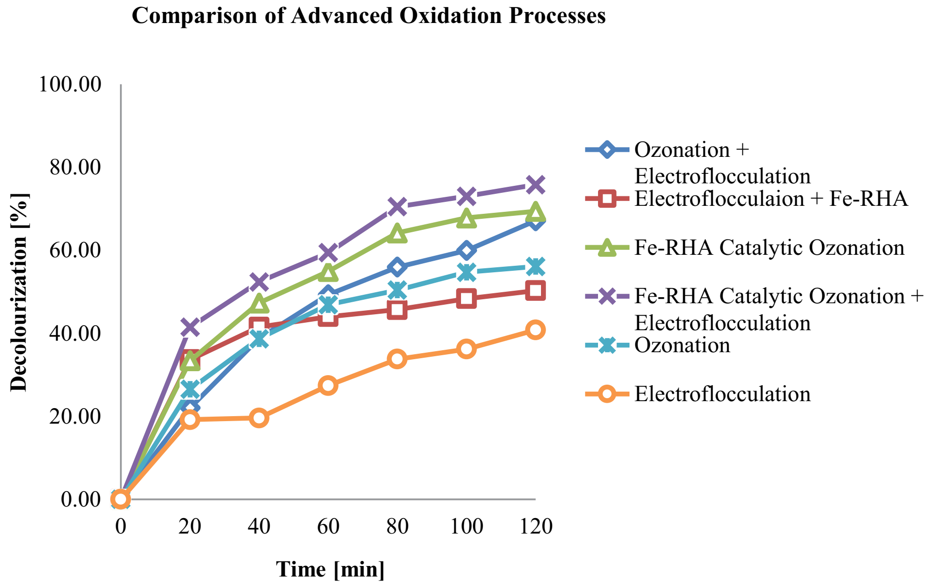


Fig. 7. Comparison of advanced oxidation processes for the decolourization of basic yellow 28 ($C_{o\,(BY)}$ = 25 mg/L; T = 30°C; catalyst amount = 40 g; V = 3,000 mL; O_3 = 0.9 mg/min; Voltage = 30 *V*; Current = 0.34 Amp; pH = 7).

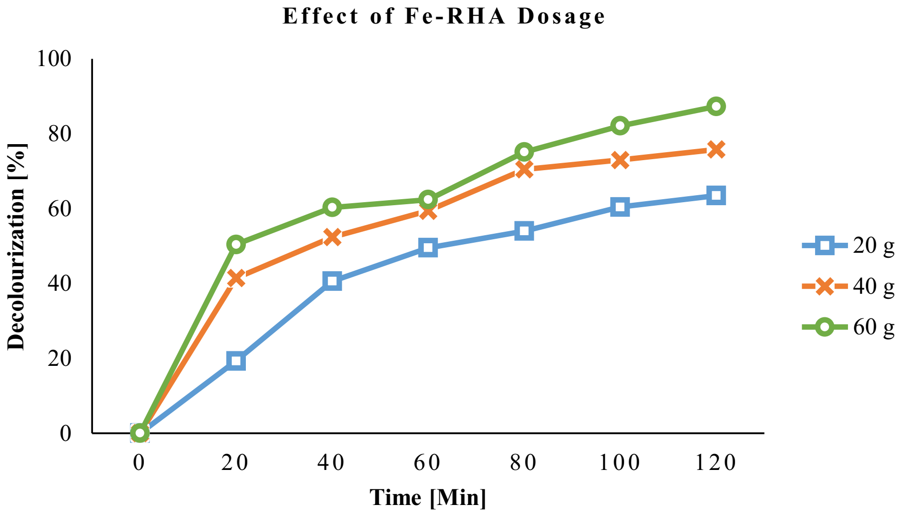


Fig. 8. Effect of Fe-RHA dosage on the decolourization of basic yellow 28 in the Fe-RHA catalytic ozonation combined with electroflocculation process ($C_{o\ (BY)}$ = 25 mg/L; T = 30°C; V = 3,000 mL; O_3 = 0.9 mg/min; Voltage = 30 V; Current = 0.34 Amp; pH = 7).

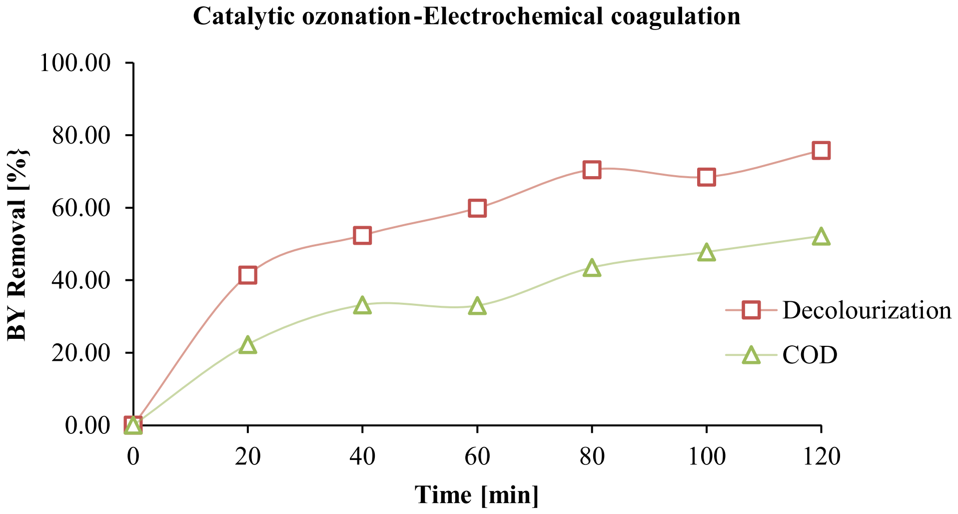
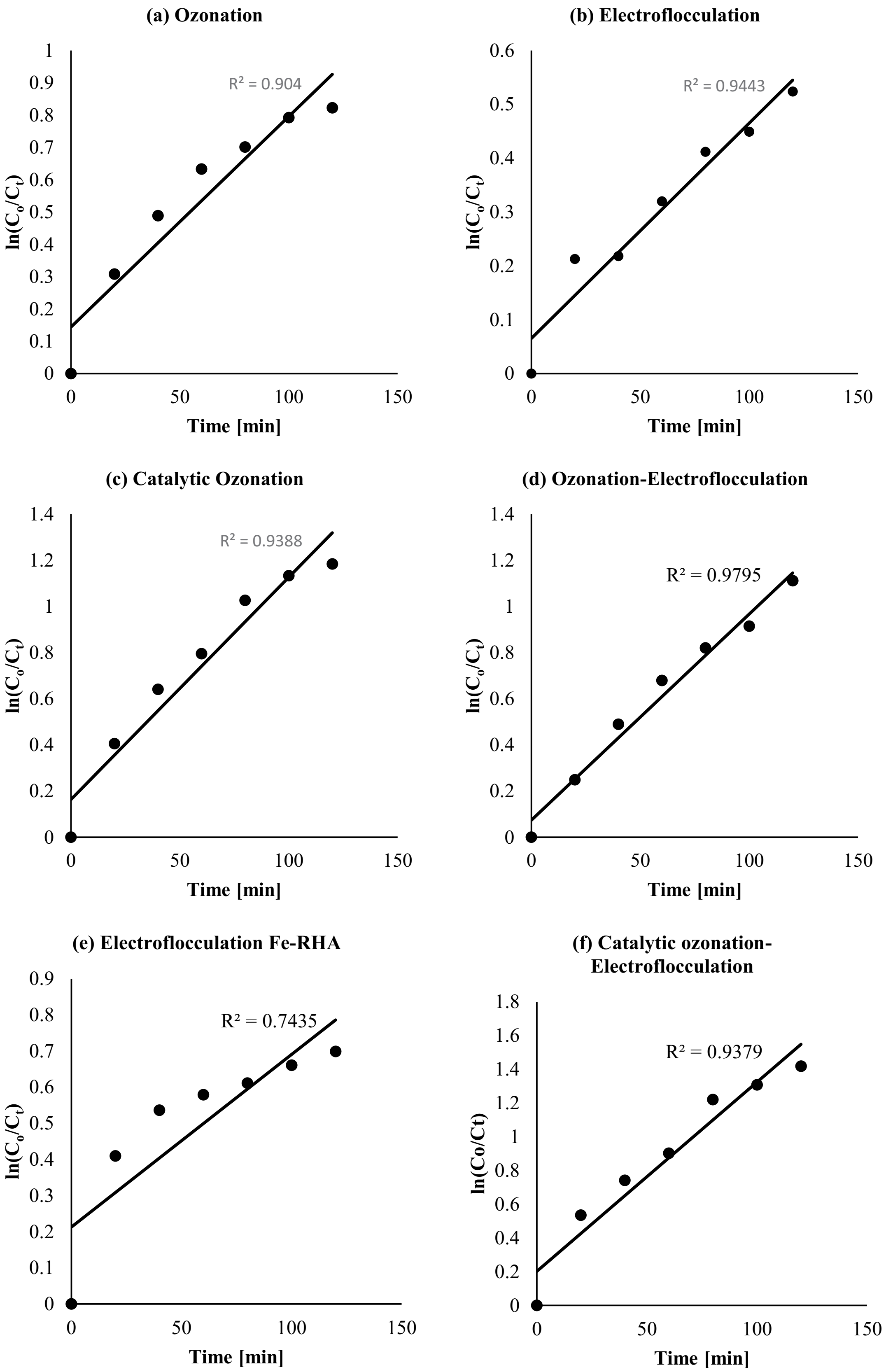


Fig. 9. Comparison of COD removal and decolourization of basic yellow 28 in the Fe-RHA catalytic ozonation combined with electroflocculation process ($C_{o\ (BY)}$ = 25 mg/L; T = 30°C; V = 3,000 mL; O_3 = 0.9 mg/min; Voltage = 30 V; Current = 0.34 Amp; pH = 7).

Table 2
Pseudo-first-order kinetic rate constants for the decolourization of basic yellow 28 ($C_{o\ (MB)}$ = 25 mg/L; T = 30°C; catalyst amount = 40 g; V = 3,000 mL; O_3 = 0.9 mg/min; voltage = 30 V; current = 0.34 Amp; pH = 7)

Process	$K \times 10^{-3}$(min^{-1})	R^2
Ozonation	6.5	0.904
Electroflocculation	4	0.944
Catalytic ozonation	9.6	0.939
Ozonation-electroflocculation	8.9	0.98
Electroflocculation-Fe-RHA	4.8	0.744
Catalytic ozonation-electroflocculation	11.2	0.938

water [20,36]. In current investigation, the integrating process was studied near neutral pH. Therefore, it was hypothesized that at studied pH the removal of BY 28 may be due to its adsorption on the gelatinous aluminium hydroxide complexes ($Al(OH)_3$ complexes) formed as a result of electroflocculation process and on the catalyst (Fe-RHA) and their subsequent reactions with adsorbed molecular ozone as well as hydroxyl radicals generated in ozonation process [20,36]. It is important to mention here that in some recent findings, it has been hypothesized that surface hydroxyl groups of iron-loaded catalysts play an important role in ozone decomposition leading to the production of hydroxyl radicals [24,37]. Previous findings further indicate that the surface of catalyst may be deprotonated when the pH of solution would be above the point of zero charge of catalyst [24,37]. Therefore, Fe-RHA (pH_{pzc} = 3.3) may be deprotonated at pH 7.0 and may acquire overall negative charge, which may lead to significant adsorption of positively



(a) Ozonation

(b) Electroflocculation

(c) Catalytic Ozonation

(d) Ozonation-Electroflocculation

(e) Electroflocculation Fe-RHA

(f) Catalytic ozonation-Electroflocculation

Fig. 10. Linear pseudo-first-order kinetic plots for the decolourization of basic yellow 28 ($C_{o\ (BY)}$ = 25 mg/L; T = 30°C; catalyst amount = 40 g; V = 3,000 mL; O_3 = 0.9 mg/min; Voltage = 30 V; Current = 0.34 Amp; pH = 7).

charge BY 28 and its subsequent removal with adsorbed ozone and hydroxyl radicals on the surface of catalyst.

4. Conclusions

- Fe-RHA catalytic ozonation was an effective method for the treatment of BY 28.
- The Fe-RHA catalytic ozonation combined with electro-flocculation was found to be the most efficient method for dye removal near wastewater pH.
- The pH effect plays an important role in determining the efficiencies of AOP.
- The kinetics of decolourization was well fitted on pseudo-first-order kinetic model.

Acknowledgements

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References

[1] A. Al-Kdasi, A. Idris, K. Saed, C.T. Guan, Treatment of textile wastewater by advanced oxidation processes – a review, Global Nest J., 6 (2004) 222–230.

[2] S. Sharma, J. Buddhdev, M. Patel, J.P. Ruparelia, Studies on degradation of reactive red 135 dye in wastewater using ozone, Procedia Eng., 51 (2013) 451–455.

[3] A. Ikhlaq, D.R. Brown, B. Kasprzyk-Hordern, Catalytic ozonation for the removal of organic contaminants in water on alumina, Appl. Catal., B, 165 (2015) 408–418.

[4] M. Kahoush, N. Behary, A. Cayla, V. Nierstrasz, Bio-Fenton and Bio-electro-Fenton as sustainable methods for degrading organic pollutants in wastewater, Process Biochem., 64 (2018) 237–247.

[5] L. Labiadh, A. Barbucci, M.P. Carpanese, A. Gadri, S. Ammar, M. Panizza, Direct and indirect electrochemical oxidation of Indigo Carmine using PbO_2 and $TiRuSnO_2$, J. Solid State Electrochem., 21 (2017) 2167–2175.

[6] A.D. Rodriguez-Lopez, J. Garcia-Garrido, C. Perez-Ramiro, E.M. Garcia-Castello, Discoloration on methylene blue solutions by direct and catalytic ozonation, J. Mater. Sci. Chem. Eng., 1 (2013) 33–38.

[7] J. Zhang, K.-H. Lee, L. Cui, T.-S. Jeong, Degradation of methylene blue in aqueous solution by ozone-based processes, J. Ind. Eng. Chem., 15 (2009) 185–189.

[8] B.S. dos Santos, E. Eyng, P.R. Stival Bittencourt, L. Mantovani Frare, É.L. de Moraes Flores, M. Budke Costa, Electro-flocculation associated with the extract of *Moringa oleifera* Lam as natural coagulant for the removal of reactive blue 5G dye, Acta Sci. Technol., 38 (2016) 483–488.

[9] A.K. Verma, R.R. Dash, P. Bhunia, A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters, J. Environ. Manage., 93 (2012) 154–168.

[10] D. Sarkar, A. Bandyopadhyay, Adsorptive mass transport of dye on rice husk ash, J. Water Resour. Prot., 2 (2010) 424–431.

[11] N.K. Daud, B.H. Hameed, Decolorization of Acid Red 1 by Fenton-like process using rice husk ash-based catalyst, J. Hazard. Mater., 176 (2010) 938–944.

[12] K.-K. Yan, J. Huang, X.-G. Chen, S.-T. Liu, A.-B. Zhang, Y. Ye, M. Li, X. Ji, Fixed-bed adsorption of methylene blue by rice husk ash and rice husk/$CoFe_2O_4$ nanocomposite, Desal. Wat. Treat., 57 (2015) 12793–12803.

[13] M.T. Yagub, T.K. Sen, S. Afroze, H.M. Ang, Dye and its removal from aqueous solution by adsorption: a review, Adv. Colloid Interface Sci., 209 (2014) 172–184.

[14] M.W. Ashraf, Removal of methylene blue dye from wastewater by using supported liquid membrane technology, Polish J. Chem. Technol., 18 (2016) 26–30.

[15] M. Bielska, J. Szymanowski, Removal of methylene blue from waste water using micellar enhanced ultrafiltration, Water Res, 40 (2006) 1027–1033.

[16] M.A. Khan, Z.A. Alothman, M. Naushad, M.R. Khan, M. Luqman, Adsorption of methylene blue on strongly basic anion exchange resin (Zerolit DMF): kinetic, isotherm, and thermodynamic studies, Desal. Wat. Treat., 53 (2013) 515–523.

[17] S. Karcher, A. Kornmüller, M. Jekel, Anion exchange resins for removal of reactive dyes from textile wastewaters, Water Res., 36 (2002) 4717–4724.

[18] Z. Chen, H. Chen, X. Pan, Z. Lin, X. Guan, Investigation of methylene blue biosorption and biodegradation by *Bacillus thuringiensis* 016, Water Air Soil Pollut., 226 (2015) 1–8.

[19] C. López-López, J. Martín-Pascual, J.C. Leyva-Díaz, M.V. Martínez-Toledo, M.M. Muñío, J.M. Poyatos, Combined treatment of textile wastewater by coagulation–flocculation and advanced oxidation processes, Desal. Wat. Treat., 57 (2015) 13987–13994.

[20] C.E. Barrera Díaz, N. González-Rivas, The use of Al, Cu, and Fe in an integrated electrocoagulation-ozonation process, J. Chem., 2015 (2015) 1–6.

[21] A.L. Torres-Sánchez, S.J. López-Cervera, C. de la Rosa, M. Maldonado-Vega, M. Maldonado-Santoyo, J.M. Peralta-Hernández, Electrocoagulation process coupled with advance oxidation techniques to treatment of dairy industry wastewater, Int. J. Electrochem. Sci., 9 (2014) 6103–6112.

[22] J. Behin, N. Farhadian, M. Ahmadi, M. Parvizi, Ozone assisted electrocoagulation in a rectangular internal-loop airlift reactor: application to decolorization of acid dye, J. Water Process Eng., 8 (2015) 171–178.

[23] R. Pode, Potential applications of rice husk ash waste from rice husk biomass power plant, Renewable Sustainable Energy Rev., 53 (2016) 1468–1485.

[24] J. Wang, Z. Bai, Fe-based catalysts for heterogeneous catalytic ozonation of emerging contaminants in water and wastewater, Chem. Eng. J., 312 (2017) 79–98.

[25] F. Adam, T.-S. Chew, J. Andas, A simple template-free sol–gel synthesis of spherical nanosilica from agricultural biomass, J. Sol-Gel Sci. Technol., 59 (2011) 580–583.

[26] Y. Flores, R. Flores, A.A. Gallegos, Heterogeneous catalysis in the Fenton-type system reactive black 5/H_2O_2, J. Mol. Catal. A: Chem., 281 (2008) 184–191.

[27] G. Ersöz, Fenton-like oxidation of Reactive Black 5 using rice husk ash based catalyst, Appl. Catal., B, 147 (2014) 353–358.

[28] T. Preočanin, N. Kallay, Point of zero charge and surface charge density of TiO_2 in aqueous electrolyte solution as obtained by potentiometric mass titration, Croat. Chem. Acta, 79 (2006) 95–106.

[29] A.D. Eaton, E.W. Rice, A.E. Greenberg, Standard Methods for the Examination of Water and Wastewater, 21st ed., American Health Association, USA, 2005.

[30] F. Adam, J. Andas, I.A. Rahman, A study on the oxidation of phenol by heterogeneous iron silica catalyst, Chem. Eng. J., 165 (2010) 658–667.

[31] J. Lambert, M.M. Vega, E. Isarain-Chavez, J.M. Peralta-Hernandez, Ozone and electrocoagulation processes for treatment of dye in leather industry wastewater: a comparative study, Int. J. Emerg. Technol. Adv. Eng., 3 (2013) 1–9.

[32] K.A. Adegoke, O.S. Bello, Dye sequestration using agricultural wastes as adsorbents, Water Resour. Ind., 12 (2015) 8–24.

[33] D. Gümüş, F. Akbal, A comparative study of ozonation, iron coated zeolite catalyzed ozonation and granular activated carbon catalyzed ozonation of humic acid, Chemosphere, 174 (2017) 218–231.

[34] D. Polat, İ. Balcı, T.A. Özbelge, Catalytic ozonation of an industrial textile wastewater in a heterogeneous continuous reactor, J. Environ. Chem. Eng., 3 (2015) 1860–1871.

[35] E.K. Osman Gulnaz, F. Matyar, H. Cakici, Decolorization of the textile dyes reactive blue 220, acid red 414 and basic yellow 28 by ozone and biodegradation of oxidation products, Fresenius Environ. Bull., 21 (2012) 808–813.

[36] A. Ikhlaq, D.R. Brown, B. Kasprzyk-Hordern, Mechanisms of catalytic ozonation: an investigation into superoxide ion radical and hydrogen peroxide formation during catalytic ozonation on alumina and zeolites in water, Appl. Catal., B, 129 (2013) 437–449.

[37] T. Zhang, C. Li, J. Ma, H. Tian, Z. Qiang, Surface hydroxyl groups of synthetic α-FeOOH in promoting OH generation from aqueous ozone: property and activity relationship, Appl. Catal., B, 82 (2008) 131–137.