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# TOC removal from Methylene Blue aqueous solutions by adsorption and oxidation in the presence of coal fly ash

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## ABSTRACT

Total organic carbon (TOC) removal from Methylene Blue aqueous solutions in the presence of coal fly ash was experimented comparing adsorption alone with oxidation potentially catalyzed by ash carried out with oxygen or ozone-enriched oxygen flow. The experiments were performed in continuous stirred tank reactor with fixed amounts of ash and dye solution, while gaseous flow was continuously bubbled in the solution. The results of TOC removal from 20 mg/L Methylene Blue aqueous solution showed that in the case of adsorption alone the removal yield rose from 62 to 90% increasing ash dosage from 4.0 to 8.0 g/L. However, in oxygen flow only the removal with 4.0 g/L increased up to 72% and attained about 80% with ozone-enriched oxygen, yielding the best final values of TOC removed per unit mass of ash of 2.19 and 2.38 mg/g, respectively. The kinetic results have been satisfactorily fitted by a pseudo-second-order model yielding a kinetic constant which strongly increased in adsorption alone increasing ash dosage, while a further increase with oxygen was observed only for 4.0 g/L of ash. In the treatment with ozone, the removal process was slowed down.

*Keywords:* Coal fly ash; Methylene Blue; TOC removal; Adsorption; Oxidation; Ozone

## 1. Introduction

Textile dyeing and finishing industries use large amounts of water and the resulting effluents are loaded with a variety of pollutants: dyes, surfactants, heavy metals, and finishing agents. Many of these substances do not undergo biodegradation by conventional processes of treatment with activated sludges and tertiary processes of removal are required prior to discharge or recycle water in the same industry.

The removal can be accomplished by a physical process such as adsorption or reverse osmosis, but such methods, which are non-destructive and transfer pollutants to other media, involve issues of regeneration and disposal. On the other hand, the organic substances can be degraded by a strong chemical treatment such as chlorination, but with other environment damages. Instead, the so-called Advanced Oxidation Processes are aimed to produce *in situ* $HO^{\bullet}$ radicals, which have the greatest oxidation potential in comparison with other oxidants; therefore many articles have been published about the application of these processes to treatment of textile wastewaters [1]. Among them, ozonation has been widely studied since ozone has been recognized very effective to decolorize textile effluents [2] and it is known that $HO^{\bullet}$ radicals resulting from ozone decomposition in water are more reactive than ozone itself [3]. However, it has been

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reported that ozone alone is not very efficient for COD removal [4].

On the contrary, Zaror [5] observed that ozonation of toxic phenolic compounds in the presence of granular activated carbon (GAC) reduced the specific ozone consumption to about half of its value, as compared with ozonation in the absence of adsorbent. Moreover, Gül et al. [3] have proved that coupling ozonation and adsorption on activated carbon to be efficient in removing color and some of the organic matter from highly colored effluents. Faria et al. [6] studied the catalytic activities of activated carbon and cerium oxide in ozonation processes for decolorization and mineralization of solutions of dyes. They observed that with an initial dye concentration of 50 mg/L the complete decolorization was achieved by uncatalyzed ozonation in less than 10 min, but the complete removal of total organic carbon (TOC) needed 2 h in the presence of ceria-activated carbon composite, which allowed the highest removal yields. Therefore, the oxidative degradation of dyes by ozone can be significantly improved in the presence of an adsorbent with a catalytic activity.

On the other hand, many works have been carried out in order to substitute activated carbon with low-cost adsorbents for sustainable treatment of wastewaters resulting from the textile dyeing industry. Among these materials, coal fly ash originated in large amount in combustion processes and waste product of thermal power plants has been considered [7–9]. Our recent work [10] was aimed to perform continuous flow experiments of adsorption of acid or basic dye on raw fly ash in order to determine the optimum conditions to obtain the highest yields of dye removal from solutions at low concentrations (5–20 mg/L). Beyond the adsorption, fly ash could provide active components such as $SiO_2$, $Al_2O_3$, and $Fe_2O_3$, able to catalyze gas-phase and aqueous-phase oxidation of organics [11]. In particular, the catalytic activity of fly ash toward oxidations with hydrogen peroxide was studied [12,13], while the performance of fly ash was recognized closer to that of common catalysts in wet air oxidation of pulp and paper mill effluents [14]. The potential use of coal fly ash as heterogeneous catalyst in peroxidative decolorization of aqueous solution of several reactive, acid and chrome dyes using hydrogen peroxide was experimented by Sur et al. [15], while the effects of various parameters on the same reaction were studied successively [16]. Chatterjee et al. [17] experimented adsorption and photocatalysis in color removal from wastewater using fly ash and sunlight, while Flores et al. [18] used $Fe^{3+}$ containing ashes as heterogeneous catalyst in Fenton-type system to degrade a reactive dye.

Most of the studies on dye removal took into account the decolorization, but this effect can be due to adsorption and in the case of oxidation it may be limited to breaking of conjugations or molecular fragmentation without complete mineralization of the dyes. Instead the present work was aimed to perform experiments of TOC removal from Methylene Blue aqueous solutions comparing adsorption alone on fly ash with oxidation potentially catalyzed by the same and carried out with oxygen or even with ozone-enriched oxygen flow. The experiments were performed in batch mode in continuous stirred tank reactor (CSTR) with fixed amounts of ash and dye solution, while gaseous flow was, in case of need, continuously bubbled in the solution. TOC was monitored with an automatic analyzer in order to determine residual organic matter in solution.

## 2. Materials and methods

### 2.1. Materials

The coal fly ash used was kindly supplied by ENEL (Italian Electricity Company), power plant of Vado Ligure (SV, Italy). The results of chemical analysis and particle size performed by Malvern Laser Particle Sizer were reported in the previous article [10]. Moreover, the BET surface area measured by a Micromeritcs Accusorb 2100E apparatus was 7.4 $m^2/g$.

Methylene Blue (Basic Blue 9, C.I. 52015) thiazine dye (MW 319.85) was Carlo Erba product, 98.5% purity. A standard solution of 20 mg/L dye, corresponding to 12 mg/L TOC, was used in all the experiments.

### 2.2. Treatment tests

The experiments were carried out in CSTR containing a fixed concentration of ash ($m = 4.0$ or 8.0 g/L) and a solution volume of 12.00 L. The solution was thermostated at 20°C by an external circulating bath. The speed of the mechanical stirrer was kept at 240 rpm in order to maintain a homogeneous dispersion of the ash in the liquid. In the experiments carried out with bubbling gas, a constant gas flow (6 L/min) of oxygen or ozone-enriched oxygen was adjusted through a flowmeter. In such condition, the ozone flow rate supplied by the ozonizer apparatus (Ozolight, Turin, Italy) was 4.40 mg/min yielding 0.73 mg $O_3$/L of gas. This value was determined by reaction with potassium iodide solution buffered by phosphate. The gas flow was bubbled through a porous fritted glass fixed at the bottom of the vessel. The schematic plan of the equipment is shown in Fig. 1. The treatment time was prolonged until a

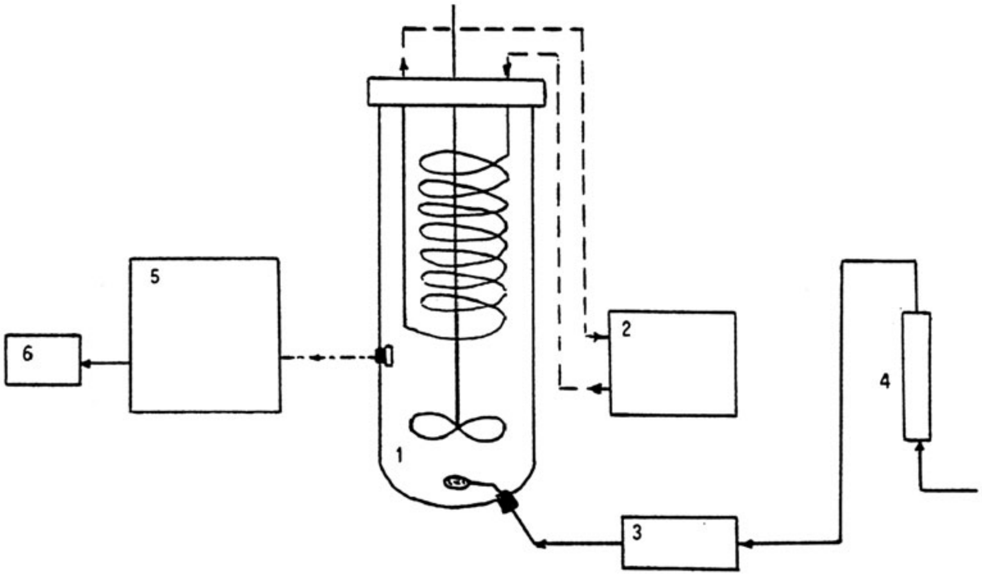

Fig. 1. Schematic plan of the laboratory plant used for the experiments. (1) CSTR, (2) thermostatic bath, (3) ozone generator, (4) gas flow meter, (5) TOC analyzer, and (6) recorder.

constant value of residual TOC was obtained, practically within 360 and 720 min.

### 2.3. TOC analyzer unit

The analysis of TOC content was performed by a TCM 400/P of Carlo Erba Strumentazione (Rodano, Italy). Such apparatus enables the determination of TOC through oxidation of the organic substances to carbon dioxide in a catalytic oven. The oxidant is a 3% aqueous solution of nitric acid. The resulting carbon dioxide is converted to methane in a methanation oven and cromatographically revealed by a FID. The apparatus enables a peak output on a recorder each 5 min and the calibration is performed by standard potassium phthalate solutions in the range of 5–100 mg/L of TOC. In this range the percentage standard deviations of repeated measurements are within 2–5%.

The sampling of the solution was carried out by a peristaltic pump which continuously withdrew a small solution flow, about 1 mL/min, through a Teflon tube (5 mm external diameter). To avoid withdrawal of ash, a small filter of cellulose acetate 0.45 μm porosity, was inserted at the beginning of the sampling tube.

## 3. Results and discussion

### 3.1. pH measurements

The coal ash used, according to ASTM C618, was of type F, since it contained more than 70 wt.% of $SiO_2 + Al_2O_3 + Fe_2O_3$ and low calcium content (8.2 wt.% of CaO) with a substantial amount of unburned carbon. In the previous article, [10] the influence of alkali release from fly ash on the pH of distilled water was tested by varying time and ash dosage $m$ in the range from 2 to 20 g/L. A strong basic character of the used ash was observed and the alkali release moderately increased with increasing ash dosage and contact time, but at low $m$ the pH values after 1 h were very close to that after 6 h (from 11.1 to 11.2 with 4.0 g/L and from 11.3 to 11.4 with 8.0 g/L). In the present work, such pH value was not modified and after treatment significant pH variations were not observed owing to the low concentration of dye removed in comparison with the ash dosage.

### 3.2. TOC removal tests

The kinetic results of TOC removal in the different conditions are compared in Fig. 2 where the residual TOC at time $t$ ($TOC_t$ mg/L) was plotted in function of treatment time. For clarity, only experimental points each 30 min interval were plotted.

Looking at the results of adsorption alone, with $m = 4.0$ g/L the removal attained 62% of initial TOC, while with $m = 8.0$ g/L the removal increased to about 90%. These values were reached within 240 min and the removal kinetics was improved at the highest $m$. Moreover, a residual TOC remaining even after longer times showed that saturation values were attained in both cases.

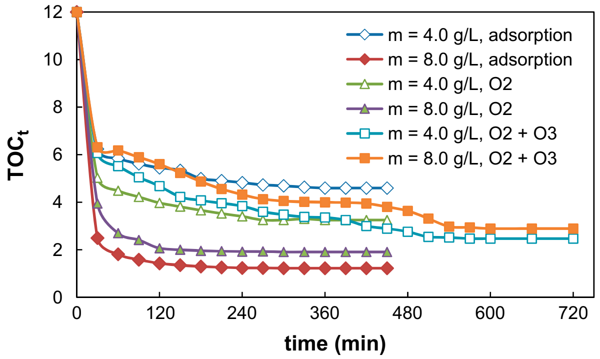

Fig. 2. Kinetic curves of TOC removal from solution of 20 mg/L Methylene Blue in the presence of fly ash in different conditions.

In the presence of oxygen flow the removal with $m = 4.0$ g/L increased up to 72%, while with $m = 8.0$ g/L the removal slightly decreased with respect the adsorption alone.

However in the presence of ozone, the removal behavior resulted more complex. In fact with both ash concentrations the removal kinetics was initially slower than that observed with oxygen alone and after about 240 min a plateau is reached; afterward TOC removal increased toward a final practically constant value. In the last case the ash concentration of 4.0 g/L yielded the higher value of about 80% of TOC removal, while with 8.0 g/L it was limited to 78%, lower than the adsorption alone and in the presence of oxygen flow. In all the experiments with gas flow, residual TOC amounts remained even after long treatment times.

### 3.3. TOC removal kinetics

The experimental results of TOC removal kinetics were fitted to the Lagergren's pseudo-first-order and Ho's pseudo-second-order models, respectively, but only the latter yielded satisfactory fitting.

The linear pseudo-second-order equation was applied in the following form:

$$\frac{t}{(\mathrm{TOC_{rem}})_t} = \frac{1}{K_2 \mathrm{TOC_e^2}} + \frac{1}{\mathrm{TOC_e}} t \tag{1}$$

where $(\mathrm{TOC_{rem}})_t$ means TOC removed at time $t$ per unit mass of ash (mg/g) calculated from the difference between initial and residual TOC in solution; $K_2$ is the rate constant of the equation (g/mg•min) and $\mathrm{TOC_e}$ the equilibrium value of TOC removed per unit mass of ash (mg/g). The results obtained by interpolation are summarized in Table 1 together with the experimental values of $\mathrm{TOC_e}$. The squared correlation coefficients ($R^2$) are very close to 1 in particular for adsorption alone and for treatment in oxygen flow, less satisfactory although acceptable for oxygen + ozone. Moreover, a good agreement was observed between calculated and experimental $\mathrm{TOC_e}$ values. In any case, the values of $\mathrm{TOC_e}$ reported in Table 1 can be considered as a measure of the exploitation of the fly ash, and the higher values were obtained with the lowest ash dosage in both the experiments with oxygen and ozone.

The comparison of $K_2$ values confirmed the trend already observed from the results of the curves plotted in Fig. 2 with the highest value for $m = 8.0$ g/L in the case of adsorption alone, lower in oxygen treatment, while for $m = 4.0$ g/L the constant is higher in oxygen flow than with adsorption alone. The lowest values of $K_2$ were found with ozone with both the ash dosages.

Strictly speaking the pseudo-second-order kinetic model should be applied to the results of dye adsorption alone, while in the experiments with oxygen flow and still even with oxygen + ozone the species generated from the dissolved gases can compete with dye molecules and oxidized products toward adsorption on the ash sites. Moreover, the ash components are able to catalyze the ozone decomposition in the early stages of treatment.

Table 1
Interpolation results according to the pseudo-second-order kinetic model

| | Adsorption | | Oxygen flow | | Oxygen + ozone flow | |
|---|---|---|---|---|---|---|
| $m$ (g/L) | 4.0 | 8.0 | 4.0 | 8.0 | 4.0 | 8.0 |
| $R^2$ | 0.9995 | 0.9999 | 0.9997 | 0.9999 | 0.9973 | 0.9929 |
| $\mathrm{TOC_{e,calc.}}$ (mg/g) | 1.93 | 1.36 | 2.26 | 1.28 | 2.53 | 1.21 |
| $\mathrm{TOC_{e,exp.}}$ (mg/g) | 1.85 | 1.35 | 2.19 | 1.26 | 2.38 | 1.14 |
| $K_2$ (g/mg min) | 0.0303 | 0.2083 | 0.0349 | 0.1535 | 0.0085 | 0.0139 |

Gül et al. [3] observed that the degradation of dyes by ozonation in the presence of GAC takes place in the bulk of the solution by the reaction of organic substances with reactive hydroxyl radicals formed on the surface of GAC; moreover the mass ratio of GAC to organic substrate in the aqueous solution should yield an optimum value for effective degradation of the organic substrates, while an excess of GAC inhibits degradation reactions probably because of adsorption of organic species on the surface of GAC. A similar mechanism can be hypothesized in the presence of fly ash in order to explain the worse results in ozonation with $m = 8.0$ g/L in comparison with $m = 4.0$ g/L.

## 4. Conclusion

The results of TOC removal from 20 mg/L Methylene Blue aqueous solution in the presence of fly ash showed that in the case of adsorption alone the removal yield is strongly increased by ash dosage increase from 62% with $m = 4.0$ g/L up to 90% with $m = 8.0$ g/L. However, in the treatment with oxygen flow the removal with $m = 4.0$ g/L increased up to 72% and attained about 80% with ozone-enriched oxygen, yielding the best final values of TOC removed per unit mass of ash of 2.19 and 2.38 mg/g, respectively. Instead with $m = 8.0$ g/L the corresponding values with oxygen and ozone are lower than in the case of adsorption alone. The kinetic results have been satisfactory fitted by a pseudo-second-order model yielding a kinetic constant which strongly increased in adsorption alone moving from $m = 4.0$ to 8.0 g/L. With oxygen a further increase was observed only with $m = 4.0$ g/L, while at the highest ash dosage the removal was slower than with adsorption alone. In the treatment with ozone the process was further slowed down.

Therefore, the optimal removal conditions were achieved with $m = 4.0$ g/L in oxygen flow where a good fly ash exploitation was coupled with an acceptable velocity, while the ozone addition yielded a little increase in exploitation but with a significant removal slackening.

## References

[1] I. Arslan, I.A. Balcioğlu, Degradation of commercial reactive dyestuffs by heterogenous and homogenous advanced oxidation processes: A comparative study, Dyes Pigm. 43 (1999) 95–108.

[2] K.D. Inaloo, K. Naddafi, A.R. Mesdaghinia, S. Nasseri, R.N. Nodehi, A. Rahimi, Optimization of operational parameters for decolorization and degradation of C.I. Reactive Blue 29 by ozone, Iran. J. Environ. Health Sci. Eng. 8 (2011) 227–234.

[3] Ş. Gül, Ö. Özcan, O. Erbatur, Ozonation of C.I. Reactive Red 194 and C.I. Reactive Yellow 145 in aqueous solution in the presence of granular activated carbon, Dyes Pigm. 75 (2007) 426–431.

[4] L. Szpyrkowicz, C. Juzzolino, S.N. Kaul, A comparative study on oxidation of disperse dyes by electrochemical process, ozone, hypochlorite and Fenton reagent, Water Res. 35 (2001) 2129–2136.

[5] C.A. Zaror, Enhanced oxidation of toxic effluents using simultaneous ozonation and activated carbon treatment, J. Chem. Technol. Biotechnol. 70 (1997) 21–28.

[6] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, Activated carbon and ceria catalysts applied to the catalytic ozonation of dyes and textile effluents, Appl. Catal., B 88 (2009) 341–350.

[7] M. Visa, F. Pricop, A. Duta, Sustainable treatment of wastewaters resulted in the textile dyeing industry, Clean Technol. Environ. Policy 13 (2011) 855–861.

[8] M. Matheswaran, Kinetic studies and equilibrium isotherm analyses for the adsorption of Methyl Orange by coal fly ash from aqueous solution, Desalin. Water Treat. 29 (2011) 241–251.

[9] S. Dubey, S. Uma, L.Sujarittanonta, Y.C.Sharma, Application of fly ash for adsorptive removal of malachite green from aqueous solutions, Desalin. Water Treat. 53 (2015) 91–98.

[10] F. Ferrero, Dye removal from aqueous solution using coal fly ash for continuous flow adsorption, Clean Technol. Environ. Policy (2015), doi: 10.1007/s10098-015-0908-y.

[11] S. Wang, Application of solid ash based catalysts in heterogeneous catalysis, Environ. Sci. Technol. 42 (2008) 7055–7063.

[12] D. Mallick, S. Khanra, S.K. Chaudhuri, Studies on the potential of coal fly ash as a heterogeneous catalyst in oxidation of aqueous sodium sulfide solutions with hydrogen peroxide, J. Chem. Technol. Biotechnol. 70 (1997) 231–240.

[13] S.H. Chen, D.Y. Du, Degradation of n-butyl xanthate using fly ash as heterogeneous Fenton-like catalyst, J. Cent. South Univ. 21 (2014) 1448–1452.

[14] A. Garg, S. Saha, V. Rastogi, S. Chand, Catalytic wet air oxidation of pulp and paper mill effluent, Indian J. Chem. Technol. 10 (2003) 305–310.

[15] B. Sur, S. Mandal, S.K. Chaudhuri, Fly ash—A potential heterogeneous catalyst in peroxidative degradation of aqueous dye solutions, Indian J. Eng. Mater. Sci. 3 (1996) 119–123.

[16] S.K. Chaudhuri, B. Sur, Oxidative decolorization of reactive dye solution using fly ash as catalyst, J. Environ. Eng. 126 (2000) 583–594.

[17] D. Chatterjee, B. Ruj, A. Mahata, Adsorption and photocatalysis of colour removal from waste water using fly ash and sunlight, Catal. Commun. 2 (2001) 113–117.

[18] 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.