Reactive dye removal by paper mill sludge impregnated with iron (III)

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Abstract. This paper presents evaluation of the possibility of using Fe-impregnated paper mill sludge (Fe-PS) in the heterogeneous Fenton process of anthraquinone Reactive Blue 4 (RB4) dye removal. In order to determine the effectiveness of the oxidation process, experiments were carried out in two stages: (i) adsorption of RB4, and (ii) oxidation through a Fenton process. The percentage of dye removal by adsorption, and adsorption followed by Fenton process was 82.0, and 90.9%, respectively. Adsorption and degradation kinetics indicate higher reaction rate of decolorization by Fenton process. The content of iron leached into solution after Fenton process was 0.29 mg/L. These results provide basis for further investigation of paper mill sludge application in terms of optimization of Fenton reaction conditions, reuse of material and assessment of solution toxicity.

Keywords: paper mill sludge, reactive dye, Fenton process

1. Introduction

Textile processing generates numerous waste streams, including waste water. Most of the chemicals and auxiliaries, looking at the entire life cycle of the product, is discharged through the waste water into the environment. Unfixed coloring agents are one of the pollutants that are released through the waste water during the dyeing and finishing of textiles. Poor fixation of dyes has been a long-standing problem in terms of reactive dyes, and that in the discontinuous dyeing processes of cellulose fibers. High temperatures have an effect on improving color washout, therefore, a large number of factories use warm wash of unfixed hydrolysed reactive dyes, thus avoiding the use of detergents in this phase but increases the possibility of their release into waste water. For the textile finishing industry, advanced oxidation with a Fenton-like reaction is proposed as a viable pretreatment technique (EC, 2003). From the standpoint of industrial applications, heterogeneous Fenton processes are conceptually attractive because it does not require the step of separation of sludge, which is a main disadvantage of the homogeneous Fenton process (Dantas *et al*., 2006). In a homogeneous phase, the chemical changes that take place depend on the nature of interaction of responders in a Fenton's reagent with compounds that are degraded (Neyens and Baeyens, 2003). However, in a heterogeneous phase, in addition to chemical changes, occurring further physical changes to the active sites on the catalyst surface. At the end of the reaction, the product molecules are desorbed and leave the active sites which are then available to the new molecules of the reactants to adsorb on the surface and react (Blanco *et al*., 2014). Application of the heterogeneous catalysts of Fenton-type is an alternative which can allow the operation in the conventional reactors, without the use of soluble salts of iron (Chaliha and Bhattacharyya, 2008), wherein the catalyst is stable and can be reused in the process.

Most common case of industrial symbiosis is productive use of a material stream by one entity that is regarded as waste by another entity. Until today, various methods of disposal or use of paper mill sludge (PS) were adopted, which are essential for the development of economically and environmentally acceptable methods in order to increase the recovery of useful materials in and/or energy, which leads to minimization of waste sludge from the paper industry. In this context, several research studies have shown that PS as waste material can be directly or indirectly (converting it into activated carbon) used as a active sorbent (Calisto *et al*., 2014; Likon and Trebše, 2012; Méndez*et al*., 2010).

In this work was examined the application of modified paper mill sludge in the adsorption and oxidation processes (heterogeneous Fenton reaction). Impre-gnation technique with Fe(III) ions was used for producing an active catalyst. The decolorization of an aqueous solution of synthetic Reactive Blue 4 dye was followed during 180 minutes, and also the removal of total organic carbon (TOC).

2. Methods

2.1. Materials

All chemicals used in the experiments were supplied from Sigma-Aldrich Company (Germany), and those are: H_2O_2 (30%, w/w), 95-97% H_2SO_4, Na_2CO_3, $Fe(NO_3)_3 x9H_2O$ and dye Reactive Blue 4 (RB4). Figure 1 presents the structure of RB4 dye. All solutions were prepared with deionised water. Paper mill sludge was delivered from a factory which is engaged in manufacturing of cardboard from recycled paper.
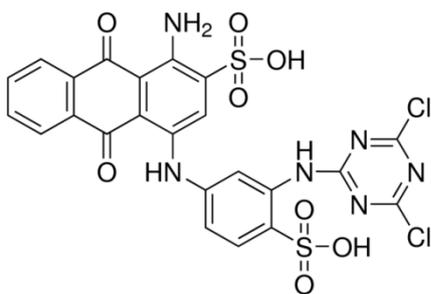
Figure 1. Structure of RB4 dye

2.2. Preparation of materials

An aqueous suspension of the raw paper mill sludge (RPS) was dried at room temperature (22°C) and grinded to a fraction 0.16 mm. Dried and crushed sludge was calcinated at a temperature of 350°C for 2 h. This sample was labelled as CPS.

A solution of a Fe precursor for paper mill sludge impregnation was prepared by vigorous stirring of the powdered Na_2CO_3 and 0.2 M solution of $Fe(NO_3)_3x9H_2O$ on the vibratory shaker (Heidolph Vibramax) for 2 hours. To a suspension of the sludge (1 g of dried sludge in 50 ml of deionised water) was slowly added a solution of Fe precursor and stirring was continued for an additional 2 h. The mixture was dried at 100°C in a water bath. The dried material was washed with deionised water to remove unfixed Fe ions from the surface of impregnated sludge and residual impurities of the sludge. After that, the material was dried in a water bath and calcinated at a 350°C, 2h. Thus prepared catalyst was designated as Fe-PS.

2.3. Characterization of materials

Materials were characterized by multi-point BET (Brunauer–Emmett–Teller) method by AutosorbiQ Surface Area Analyzer (Quantochrome Instruments, USA) in order to determine specific surface area. For examination of structural characteristics scanning electron microscopy (SEM) (TM3030, Hitachi High-Technologies, Japan) and energy dispersive spectrometry (EDS) (Brucker Quantax 70 X-ray detector system, Brucker Nano, GmbH Germany) was used. The content of leached Fe in the solution after Fenton process was determined by atomic absorption spectrophotometer (AAS) Perkin Elmer Analyst 700.

2.4. RB4 dye removal method

Comparison of the applied process was carried out under the following experimental conditions: [RB4]=50 mgL^{-1}, pH=3, [Fe-PS]=0.1 g/100 ml, for determining the adsorption/desorption equilibrium between the dye solution and Fe-PS. Secondly, hydrogen-peroxide was added to a final concentration in the solution [H_2O_2]=20mM for the initiation of Fenton process. Samples were taken at a given time intervals during the adsorption and oxidation reactions and centrifuged at 12000 RPM for 5 min to remove solid particles and was immediately analyzed thereafter. Decolorization was monitored by absorbance (A) at λ_{max}=594.78 nm (UV/VIS spectro-photometer, Shimadzu, Japan). Total organic carbon (TOC) removal was followed by LiquiTOC II (Elementar, Germany). The experiments were conducted on a jar test apparatus (FC6S Velp Scientifica, Italy).

The efficiency of color and TOC removal was obtained by the application of the following formulas:

$$100(A_0 - A_t)/A_0) = \text{color removal (\%)} \qquad (1)$$

where A_t represents absorbance after a certain reaction time and A_0 was the initial absorbance.

$$100(TOC_0 - TOC_t)/TOC_0) = \text{TOC removal (\%)} \qquad (2)$$

where TOC_t value was measured after a certain reaction time and TOC_0 was the carbon concentration of RB4 plus the TOC concentration of the Fe-PS in deionised water.

3. Results and discussion

#### 3.1. Surface characteristics of RPS, CPS and Fe-PS

The results of BET analysis indicated the small surface of raw paper sludge, 3.48 m^2/g. Differently from Zhou *et al.* (2015) who was observed a smaller specific surface after modification of paper mill sludge, in this case, after calcinations and impregnation, the surface is significantly increased to 25.6 and 78.0 m^2/g, respectively, thus providing materials with larger contact surface. It is assumed that the increase in Fe-PS surface resulted from the transformations of Fe precursor, during calcination period, into the much smaller Fe-oxide particles, which is typical for lower calcination temperature, up to 350°C (Iurascu *et al.*, 2009).

a)   b)   c)
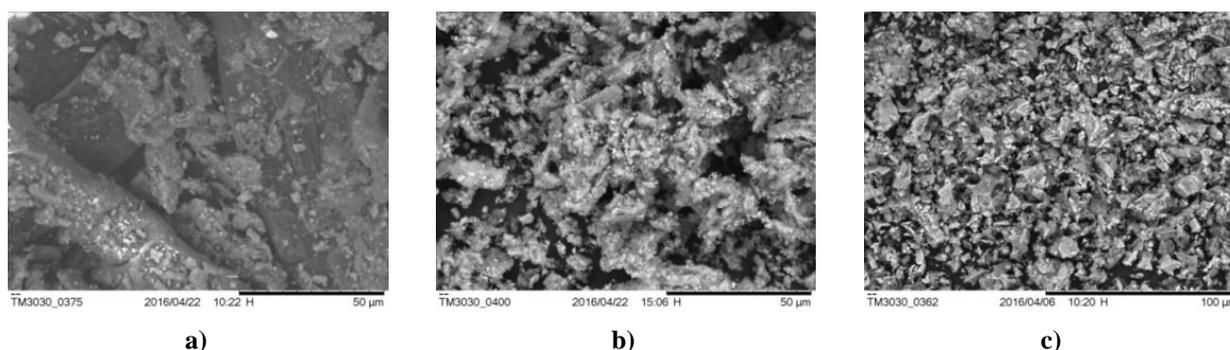
Figure 2. SEM images of a) RPS, b) CPS and c) Fe-PS
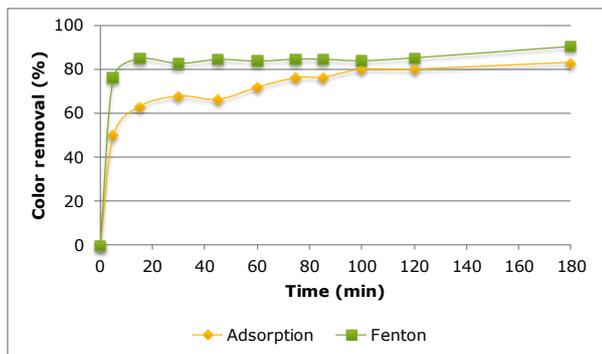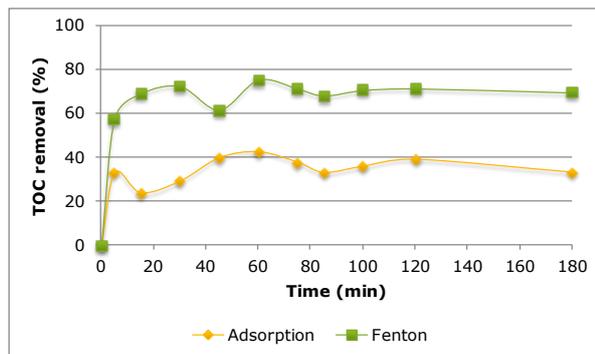
Figure 3. Efficiency of adsorption and Fenton process: a) decolourization and b) TOC removal

EDS is a convenient method for the determination of elemental composition of analyzing materials. By its implementation were confirmed a low percentage of the present iron in the RPS (0.36 wt.%) compared to the other elements and much higher (54.29 wt.%) in the Fe-PS, which indicates the modification of the starting material by the impregnation method.

SEM surface morphology analyses of raw, calcined and Fe-loaded paper mill sludge were shown on Figure 2. Sludge RPS contained significant amounts of cellulosic fibres and inorganic fillers.

Calcination process at 350°C leads to the significant changes of CPS surface and formation of pores of different sizes and shapes as a consequence of the decomposition of organic matter and the removal of present H_2O molecules (Li *et al*., 2011). Particle size distribution in Fe-PS was found to be even more uniform than for the CPS.

3.2. Efficiency of adsorption and Fenton process

The experiments were carried out using Fe-PS in the following manner: (i) adsorption of RB4, (ii) oxidation through a Fenton process. The results obtained for decolorization are shown in Fig. 3a, and indicate that the efficiency of adsorption increases with time, but with a small interval of growth. This may be explained by the fact that at the beginning of reaction all active sites are available, and then become saturated as time increases (Belaid *et al*., 2013). After 90 min of reaction and by the end of the reaction time, were not observed any significant difference in the further adsorption of the dye molecules. The percentage of dye removal by adsorption was 82.0%. When initiating the Fenton process, with Fe-PS and H_2O_2, decolorization reaching 76.5% after 5 min, and till the end of the reaction it increased up to 90.9%. Achieved high efficiency may be due to a sufficient number of active sites on the catalyst surface and also sufficient concentration of H_2O_2 as a main source of hydroxyl radicals (Lucas *et al*., 2013).

Results for TOC removal are given in Fig 3b, where higher mineralization was achieved by implementing heterogeneous Fenton process, 30% more than it was obtained by adsorption. Also, quick mineralization of RB4 dye was accomplished due to the fact that dye molecules or adsorbed intermediates on the Fe-PS surface can be attacked by hydroxyl radicals, formed on the catalyst surface (Feng *et al*., 2005).

After determining adsorption and Fenton process efficiency, another experiment was conducted, where adsorption (80 min) was followed by oxidation, adding H_2O_2 as an oxidant (Fig 4). When comparing adsorption and this combined treatment, at 180 min, the increase in the decolorization of RB4 dye was 13.8%. This is also noted at results of TOC removal. Therefore, we can assume that the heterogeneous Fenton process takes place at the catalytic surface between ·OH radicals generated at the active sites and RB4 molecules previously adsorbed on the surface (Lucas *et al*., 2013; Feng *et al*., 2005).
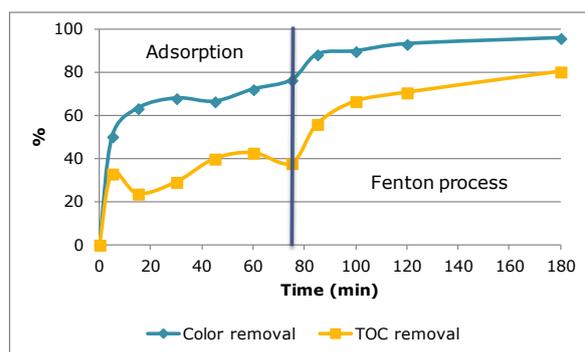
Figure 4. Combined treatment with adsorption and Fenton process

3.3. Analysis of leached iron

Throughout the analysis of leached iron in solution after the applied process it has been found that pH value had no significant effect on the stability of the applied materials. This was evidenced by the fact that during the adsorption process iron wasn't detected in the solution. But, it was found that Fenton process has an influence on leaching of iron in solution. The measured iron content in the solution after 15, 30, 60, 80 and 180 min reaction was: 0.73; 0.52; 0.34; 0.46 and 0.29 ppm. After applying combined treatment, the content of leached Fe was 0.73; 0.97; 0.58 and 0.32 ppm at 85, 100, 120 and 180 min of the Fenton reaction. So, it can be concluded that leaching of catalyst active species proceeds by a more complex mechanism than through a simple dissolution mediated by the acidic nature of aqueous solutions.

3.4. Reaction kinetics

In this work, first- (Eqs. (3)) and second-order (Eqs. (4)) reaction kinetics were used to study the decolorization rate by adsorption and Fenton process.

$$dC_t / dt = -k_1 C_t \qquad (3)$$

$$dC_t / dt = -k_2 (C_t)^2 \qquad (4)$$

where C_t is the concentration of RB4 at any reaction time; k_1 and k_2 are kinetic rate constants of first- and second order reaction kinetics, respectively; t is the reaction time. By integrating Eqs. (3) and (4), the following equations are obtained (Ertugay and Acar, 2017):

$$C_t = C_0 e^{-k_1 t} \qquad (5)$$

$$1/C_t = 1/C_0 + k_2 t \qquad (6)$$

The regression analysis was applied, based on first- and second-order reaction kinetics and results are shown in table 1. Comparing results for adsorption and Fenton process, the first-order kinetics shows smaller correlation than the second-order kinetics. Fig 5. displays values obtained for second-order kinetics.

Table 1. The parameters of kinetics models and correlation coefficients for RB4 decolorization

Model	Constants	Adsorption	Fenton
Pseudo-first order	R^2	0.942	0.652
	k_1 (min^{-1})	$2.7 \cdot 10^{-2}$	$1.75 \cdot 10^{-2}$
Pseudo-second order	R^2	0.996	0.998
	k_2 (Lg^{-1} min^{-1})	0.56	1.28
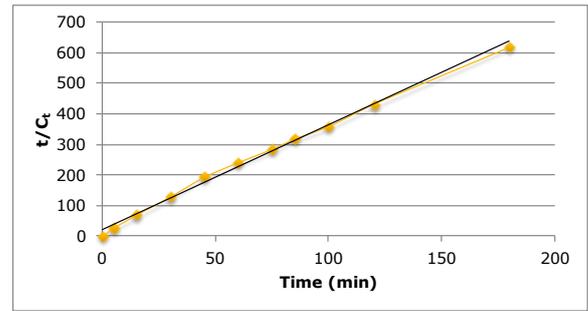
a)
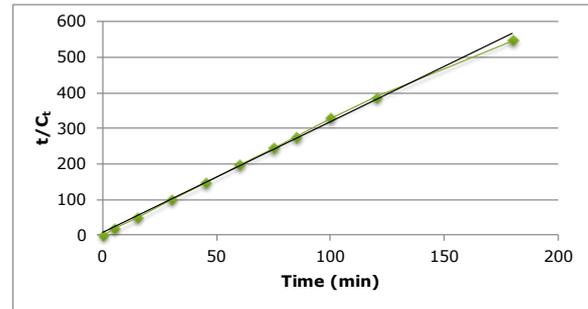
b)

Figure 5. Pseudo-second-order kinetic model for RB4 removal by: a) adsorption and b) Fenton process

References

Belaid, K.D., Kacha, S., Kameche, M. and Derriche, Z. (2013), Adsorption kinetics of some textile dyes onto granular activated carbon, *Journal of Environmental Management*, **1**, 496–503.

Calisto, V., Ferreira, C., Santos, S., Gil, M., Otero, M. and Esteves, V. (2014), Production of adsorbents by pyrolysis of paper mill sludge and application on the removal of citalopram from water., *Bioresource Technology*, **166**, 335-344.

Chaliha, S. and Bhattacharyya K.G., (2008), Catalytic wet oxidation of 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol in water with Mn(II)-MCM41. *Chemical Engineering Journal*, **139**, 575-588.

Dantas, T.L.P., Mendonça, V.P., Jose, H.J., Rodrigues, A.E. and Moreira, R.F.P.M., (2006), Treatment of textile wastewater by heterogeneous Fenton process using a new composite Fe_2O_3/carbon, *Chemical Engineering Journal*, **118**, 77–82.

Ertugay, N. and Acar, F. (2017), Removal of COD and color from Direct Blue 71 azo dye wastewater by Fenton's oxidation: Kinetic study, *Arabian Journal of Chemistry*, **10**, S1158-S1163.

European Commission, (2003), Reference Document on Best Available Techniques for Textiles Industry, Integrated Pollution Prevention and Control (IPPC), 485-499.

Feng, J., Hu, X. and Yue, P.L. (2005), Discoloration and mineralization of Orange II by using a bentonite clay-based Fe nanocomposite film as a heterogeneous photo-Fenton catalyst, *Water research,* **39**, 89-96.

Iurascu, B., Siminiceanu, I., Vione, D., Vicente, M.A. and Gil, A. (2009), Phenol degradation in water through a heterogeneous photo-Fenton process catalyzed by Fe-treated laponite, *Water research*, **43**, 1313-1322.

Li, W.H., Yue, Y.Q., Gao, Y.B., Wang, J.X., Qi, F.Y., Zhao Q.Y. and Li, J.Y. (2011), Preparation of sludge-based activated carbon made from paper mill sewage sludge by steam activation for dye wastewater treatment, *Desalination,* **278**, 179-185.

Likon, M. and Trebše, P. (2012), Recent Advances in Paper Mill Sludge Management, Industrial Waste, Prof. Kuan-Yeow Show (Ed.), InTech, DOI: 10.5772/37043.

Lucas, M., Algarra, M., Jiménez-Jiménez, J., Rodríguez-Castellón, E. and Peres, J. (2013), Catalytic activity of porous phosphate heterostructures-Fe towards Reactive Black 5 Degradation, *International Journal of Photoenergy*, **2013**, 1-6.

Méndez, A., Barriga, S., Saa, A. and Gascó, G. (2010), Removal of malachite green by adsorbents from paper industry waste material, *Journal of Thermal Analysis and Calorimetry*, **99**(3), 993–998.

Zhou, G., Chen, Z., Fang, F., He, Y., Sun, H. and Shi, H. (2015), Fenton-like degradation of Methylene Blue using paper mill sludge-derived magnetically separable heterogeneous catalyst: Characterization and mechanism, *Journal of Environmental Sciences,* **2015**, 20-26.