Journal of Hazardous Materials 244–245 (2013) 773–779

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Methyl-orange and cadmium simultaneous removal using fly ash and photo-Fenton systems

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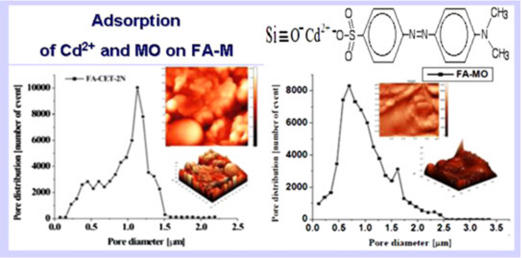
HIGHLIGHTS

- The mixed substrates of FA-M + TiO_2 proved to be highly efficient in adsorption.
- FA-M + photo-Fenton are a low-cost material for advanced treatment of wastewater.
- The adsorbed MO may act as a complexion agent, increasing the affinity for metals.
- Dye removal by photodegradation is the favourable mechanism compared to adsorption.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 April 2012
Received in revised form 8 November 2012
Accepted 8 November 2012
Available online 16 November 2012

Keywords:
Wastewater
Adsorption
Photocatalysis
Fenton-system
Fly ash

ABSTRACT

Wastewaters resulting from the textile and dye finishing industries need complex treatment for efficient removal of colour and other compounds existent in the dyeing and rising baths (heavy metals, surfactants, equalizers, etc.). Modified fly ash (FA) mixed with TiO_2 photocatalyst represent a viable option for simultaneous removal of dyes and heavy metals, and the optimized conditions are discussed in this paper for synthetic wastewaters containing methyl-orange (MO) and cadmium. For a cost-effective dye removal process, further tests were done, replacing the photocatalyst with a (photo)Fenton system. The optimized technological parameters (contact time, amount of fly ash and amount of Fe^{2+}/H_2O_2) allow to reach removal efficiencies up to 88% for the heavy metal and up to 70% for the dye. The adsorption mechanisms and the process kinetic are discussed, also considering the possibility of in situ generation of the Fenton system, due to the fly ash composition.

1. Introduction

Economic growth brings transformation, with a focus on high-tech products and domestic goods, including the dyes manufacturing and the textile finishing industries; an immediate consequence is the increase in water consumption and in wastewaters discharged into effluents. There are more than 10,000 dyes currently used in the textile industry and over 280,000 tonnes of the textile dyes are discharged every year worldwide [1]. Dyes and heavy metals are hazardous pollutants which can modify the physical and chemical properties of any ecosystem. Wastewaters resulted in the dye finishing industry have high BOD to COD values ($>2000\ mgO_2\ L^{-1}$) while the discharge limits [2,3] are much lower ($BOD < 40\ mgO_2\ L^{-1}$; $COD < 120\ mgO_2\ L^{-1}$), indicating the need for wastewater treatment, because most of the dyes are slowly or non-biodegradable.

Most of the wastewaters resulted in the dye finishing industry are also containing additives (solubility and anti-foaming agents, pH conditioners, whitening agents, etc.) and heavy metals, making the wastewater treatment complex and difficult. Toxicological studies show that the most bio-toxic heavy metal is cadmium (also

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http://dx.doi.org/10.1016/j.jhazmat.2012.11.013

Table 1
Fly ash composition.

Major oxides (wt.%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	MnO	LOI[a]
53.32	22.05	8.97	5.24	2.44	2.66	0.63	1.07	0.08	1.58

Trace elements ($mg\,g^{-1}$)

Ba	Cu	Zr	Sn	Pb	As	Ni	Zn	Ti	Cr	V	Co
700	60	100	3	35	100	55	160	6414	100	115	12

[a] Loss of ignition.

part of some metal-complex dyes), while dyes and pigments are affecting water transparency, reducing light penetration and gas solubility in water [4], also being mutagenic to human. The conventional removal processes mostly used are: chemical precipitation [5], flocculation/coagulation, membrane separation (ultrafiltration, reverse osmosis), adsorption (mainly using activated carbon), catalytic oxidation [6], and ozonation. But full colour removal has limited efficiency when both pollutants (dyes and heavy metals) are present. Supplementary, colour removal does not necessarily end up with complete de-pollution (mineralization); bleaching without demineralisation can lead to by-products more harmful (un-saturated hydrocarbons, carbonyl and carboxyl products, etc.) and fulfilling the discharge regulations [3] might be questionable.

Modified fly ash proved to be an efficient heavy metal adsorbent (Cd, Cu and Ni) [7,8], and dyes removal (methylene blue) with over 60% efficiency [9]. Mixtures of fly ash and activated carbon powder were already investigated with good results for heavy metals; average results were also obtained on these substrates for methyl-orange [8,10].

Combined substrates for a single-step process able to simultaneously remove pollutants from different classes represent a study initiated in the past years, aiming at developing up-scalable and low-cost advanced wastewater treatment processes. The efficiency of the pollutants' removal process especially methyl-orange from wastewaters loaded with dyes and heavy metals can be improved by using fly ash and TiO_2 [11] or WO_3 [12], by combining adsorption and photocatalysis.

The photocatalysis efficiency is improved by adding oxidation agents as H_2O_2 and/or Fenton systems, usually based on $Fe^{2+/3+} + H_2O_2$ [13]. In this case, three mechanisms can be expected in the system containing both, fly ash and TiO_2: adsorption, heterogeneous photocatalysis and homogeneous (photo) catalysis.

This paper investigates a combined treatment process of wastewaters with complex pollution load (heavy metals and dyes); the process includes simultaneous adsorption (FA), along with homogeneous (Fenton) and heterogeneous (TiO_2 and FA) photocatalysis. Methyl-orange (MO) was used in the experimental test because it has a remarkable stability to photo-degradation (due to the extended π-electrons delocalisation on the two aromatic rings and the adjacent groups), being therefore used as standard in many studies, while cadmium was chosen as one of the most toxic heavy metal.

2. Experimental

2.1. The substrates

Raw fly ash (FA) was collected from the electro-filters. The coal burned in power plant CHP Brasov from Romania is a mixture of coals (bituminous and pit coal). The main oxides and trace elements in the raw fly ash were identified by atomic absorption spectrometry with graphite furnace and are presented in Table 1, as given by the CHP plant.

Table 2
The surface characteristics of FA-M with TiO_2.

Component	Surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
FA-M	11.33	0.06	20.33
TiO_2	50.02	0.25	30.08

The main oxides in the fly ash composition are SiO_2 (53.7%), Al_2O_3 (21.60%) and Fe_2O_3 (9.56%); according to the ASTM standards [14], the fly ash is of F type, and it hardens or modifies only in contact with water and lime, otherwise it does not aggregate during long contact with water. Other oxides in the fly ash composition (TiO_2 1.07% and Mn_2O_3 0.08%) are important as possible participants in dyes photodegradation; the fly ash also contains unburned carbon (1.58%) representing efficient adsorption sites for dyes and heavy metals [15].

Raw fly ash was washed with ultra-pure water, by mechanical agitation (100 rpm) using Nahita GJ-1 stirrer, at room temperature (23 °C), for 48 h, to remove the soluble compounds. The ratio raw fly ash (g):ultra-pure water (mL) was 1:10. After 48 h the suspension was subject of filtration and dried at 105 °C.

Modified fly ash (FA-M): adsorption experiments on water-washed FA proved very low efficiencies in heavy metals and dyes removal as result of a low surface charge and a low specific surface. Based on previous studies [16], optimized conditions were applied to modify the fly ash surface (area and charge), by mechanical stirring (100 rpm) using Nahita GJ-1 stirrer washed FA for 48 h, at room temperature (23 °C) in NaOH 2 $mol\,L^{-1}$ solution, followed by filtration, washing with ultra pure water, drying at 105–115 °C and selecting the 40–100 μm fraction by mechanical sieving (Analysette 3 Spartan); this fraction represents 37.35 wt.% of the total FA and the rest of the ash could be further valorized in obtaining geo-polymers, in manufacturing concrete, bricks and ceramic tiles, or as filler in plastics and paints.

This fraction was selected because of two main reasons: (a) as adsorbent, a large specific surface is required (corresponding to low dimensional grains) and (b) these values still make possible up-scalable separation processes in designing the wastewater treatment process. The last reason also made us not to further mill this fraction.

This fly ash was further used in the experiments.

Mixed substrates FA-M with TiO_2 was obtained using TiO_2 Degussa P25. Degussa P25 is a mixture of anatase and rutile in a 3:1 ratio, delivered as 30 nm nano-sized particles, with a high specific surface area.

The surface characteristics, both for FA-M and TiO_2 were evaluated using a BET surface analyser (Tri Star II 3020 – Micromeritics) and are presented in Table 2.

All the experiments on mixed substrates used the previously optimized ratio FA:TiO_2 = 3:1 [11].

The FA crystalline structure was evaluated by XRD (Bruker D8 Discover Diffractometer) and AFM images (Ntegra Spectra, NT-MDT