



RECYCLABLE POROUS MATERIALS FOR THE UPTAKE OF BISPHENOL A

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Abstract: *The presence of pollutants in the environment, food, drinking water and other compounds in direct or indirect contact with humans is a major environmental issue. In this regard, a privileged place reverts to the capture or decomposition of pollutants without producing traces of residual toxins. An interesting approach for depollution is the use of natural, non-toxic, recyclable materials as adsorbents and catalysts. The aim of this work was to study the ozonation of bisphenol-A in water in the presence of Bentonite and its acid-activated counterparts AAB1, AAB4, AAB8, AAB15 and AAB24 obtained after 1, 4, 15 and 24 h of acid treatment. For comparison, one also used two deriving montmorillonite-rich materials ion-exchanged with Na⁺ and Fe²⁺ cation, namely, NaMT, Fe(II)MT. The kinetic and thermodynamic parameters of the process were assessed through UV-Vis spectrophotometric measurements, and were discussed in correlation with thermo-programmed desorption technique (TPD) data. Calculations of the retention capacities of CO₂ and H₂O (CRC and WRC) revealed high basic character (high CRC) for NaMT but lower hydrophilic character (low WRC) as compared to Fe(II)MT. This explains the higher catalytic activity of Fe(II)Mt by enhanced interaction with basic bisphenol (pka = 9.2 at 25°C), which favors adsorption, and higher dispersion in water, which offer higher contact surface as compared to NaMt. This provides valuable date for designing effective oxidative water treatments using clay materials and other natural's counterpart.*

Keywords: *bisphenol; ozonation; bentonite; montmorillonite; iron cation, thermal programmed desorption.*

1. Introduction

Bisphenol A is used in polycarbonates production as well as a precursor for epoxy resins [1]. In 2011, about 5.5 million tons of bisphenol A were produced, which were subsequently used for the manufacture of polycarbonate bottles and tableware, bottles for infant formula, and so on [[1], [2], [3]]. By multiple molecular mechanisms, bisphenol A has a strong disrupting effect on estrogenic activity, as well as other endocrine activities [[3], [5], [6], [7]]. Several studies and researches

have shown that all age categories are affected by the action of bisphenol A because it is detected in the urine of most adults is children tested [[2], [8]]. However, small children and babies are more sensitive when exposed to the action of bisphenol A. This compound has already been detected in the serum of pregnant women, breast milk, placental tissues and fetal liver, which shows that the child is exposed to the action of bisphenol A at the stage of fetal development [[2], [7], [9], [10]].

The heat and contact with any of the components, whether basic or acidic, will accelerate the hydrolysis of the ester bonds that bind bisphenol A in the polycarbonates and resins. It is the same hydrolysis and the same thermal action that takes place during the processes of pasteurization or sterilization or by microwave heating. Preheating food or even washing food containers allows bisphenol A to enter the food [[7]].

Because of increasing environmental pollution, bisphenol A has become one of the most important pollutants and the need to eliminate it is of great importance [11]. An interesting approach for pollution abatement and prevention is the use of natural, non-toxic, recyclable materials as adsorbents and catalysts [12], [12]. This approach also involves more environmentally friendly methods of synthesizing and modifying such materials that do not use or produce potential pollutants. This will certainly open up promising prospects for a more "green" chemistry for the decontamination of water used in the food, pharmaceutical and cosmetic industries as well as for environmental sanitation in general. To achieve this objective, an experimental attempt made it possible to highlight the beneficial role of the combination of ozone with a porous aluminosilic surface such as natural bentonite and montmorillonite, its purified derivative.

2. Materials and methods

To perform the experiments we used bisphenol A (2,2-Bis(4-hydroxyphenyl)propane) with the following parameters: assay – 97%, bp – 220°C/4 mmHg(lit.), mp – 158-159°C(lit.) [14]. Bisphenol A has been subjected to the ozonation process using a 20 mL aqueous solution (10^{-4} M) at different ozone exposure duration (1, 2, 3, 4, 5, 7, 10, 15,

20 and 25 minutes), using the respective ozonation: 10 mg / 1 min, 20 mg / 2 min, 30 mg / 3 min, 40 mg / 4 min, 50 mg / 5 min, 70 mg / 7 min, 100 mg / 10 min, 150 mg / 15 min, 200 mg / 20 min, 250 mg / 25 min.

To intensify the effect of ozone, one used two types of bentonite (BentA and BentB), ion exchange with sodium (NaMT) and iron (FeMT) montmorillonite, as well as bentonites having undergone treatment with sulfuric acid for 1, 4, 8, 15 and 24 hours (AAB1, AAB4, AAB8, AAB15 and AAB24). For the ozonation tests, 40 mg/L of each catalyst was previously inserted in 20 mL of bisphenol A solution, before triggering the bubbling of ozone at a rate of 6 mg / h.

The basic and hydrophilic characteristics were evaluated by thermo-programmed desorption analysis (DTP or TPD) of 40 mg of each catalyst, previously saturated with carbon dioxide and water vapor.

3. Results and discussion

The UV-Vis spectra made it possible to trace the evolution of the absorbance of each of the two spectral bands of Bisphenol A (Fig. 1, Fig. 2, Fig. 3, Fig. 4, Fig. 5).

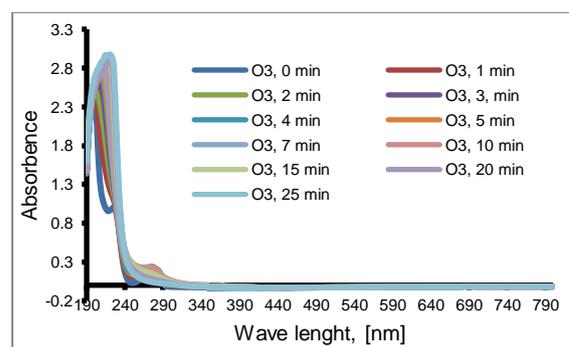


Fig. 1. Bisphenol A UV-Vis spectra at different ozonation time without catalyst: Concentration – 10^{-4} M; volume: 20 ml; ozonation regimes: 10 mg/1min, 20 mg/2 min, 30 mg/3 min, 40 mg/4 min, 50 mg/5 min, 70 mg/7 min, 100 mg/10 min, 150 mg/15 min, 200 mg/20 min, 250 mg/25 min.

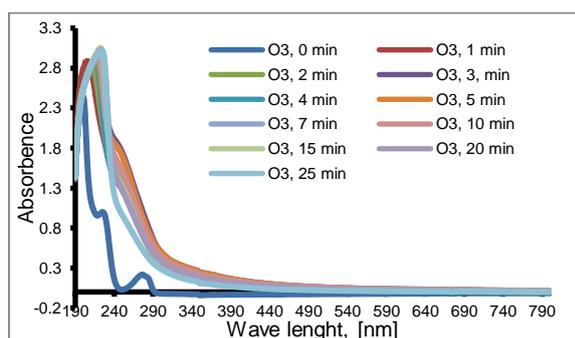


Fig. 2. Bisphenol A UV-Vis spectra at different ozonation time with Bentonite as catalyst: Concentration – 10^{-4} M; volume: 20 ml bisphenol + 40 mg BentA; ozonation regimes: 10 mg/1 min, 20 mg/2 min, 30 mg/3 min, 40 mg/4 min, 50 mg/5 min, 70 mg/7 min, 100 mg/10 min, 150 mg/15 min, 200 mg/20 min, 250 mg/25 min.

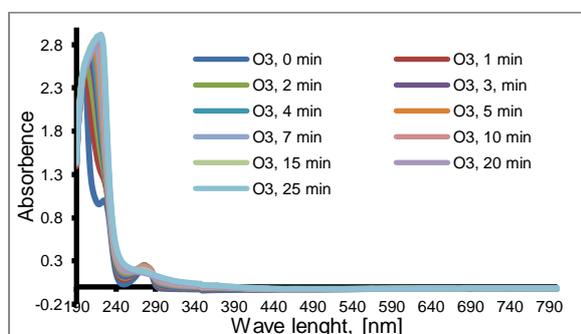


Fig. 3. Bisphenol A UV-Vis spectra at different ozonation time with FeMT as catalyst: Concentration – 10^{-4} M; volume: 20 ml bisphenol + 40 mg FeMT; ozonation regimes: 10 mg/1 min, 20 mg/2 min, 30 mg/3 min, 40 mg/4 min, 50 mg/5 min, 70 mg/7 min, 100 mg/10 min, 150 mg/15 min, 200 mg/20 min, 250 mg/25 min.

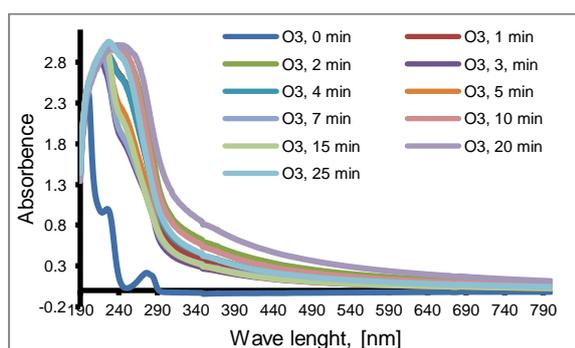


Fig. 4. Bisphenol A UV-Vis spectra at different ozonation time with NaMT as catalyst: Concentration – 10^{-4} M; volume: 20 ml bisphenol + 40 mg NaMT; ozonation regimes: 10 mg/1 min, 20 mg/2 min, 30 mg/3 min, 40 mg/4 min, 50 mg/5 min, 70 mg/7 min, 100 mg/10 min, 150 mg/15 min, 200 mg/20 min, 250 mg/25 min.

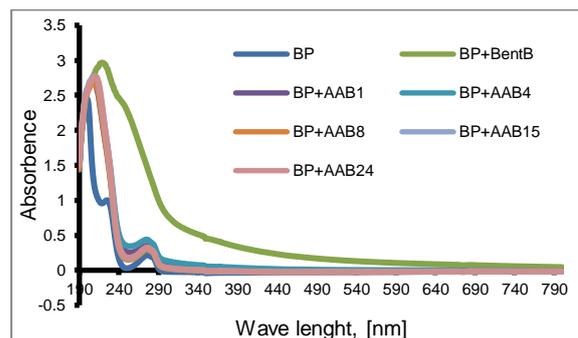


Fig. 5. Bisphenol A UV-Vis spectra at different ozonation time with Bent B, AAB1, AAB4, AAB8, AAB15 and AAB24 as catalyst: Concentration – 10^{-4} M; volume: 20 ml bisphenol + 40 mg catalyst; ozonation regimes: 50 mg/5 min.

The analysis of the UV-Vis spectra of bisphenol A subjected to the action of the ozonation process has shown that Fe (II) MT is the most effective than NaMt. This is probably due to its acidic nature, which makes it possible to retain the most basic molecule of bisphenol A ($pka = 9.2$ at $25^{\circ}C$).

This hypothesis is confirmed by the analysis of thermo-programmed desorption (TPD).

Fig. 6 Fig. 7 and others relating to Fe (II) Mt have been used to calculate the values of the CO_2 and water retention capacities (CRC and WRC). These are summarized in Table 1.

Calculations of CO_2 and water retention capacities (CRC and WRC) revealed a high basic character (high CRC) for NaMT but a lower hydrophilic character (WRC low) compared to MT Fe (II). This explains the higher catalytic activity of Fe (II) Mt by a stronger interaction with basic bisphenol ($pka = 9.2$ at $25^{\circ}C$), which promotes its adsorption, and a greater dispersion in water, which offers a contact area greater than that of NaMt in water. This provides valuable data for designing effective treatments for oxidizing water using clay materials and other natural counterparts.

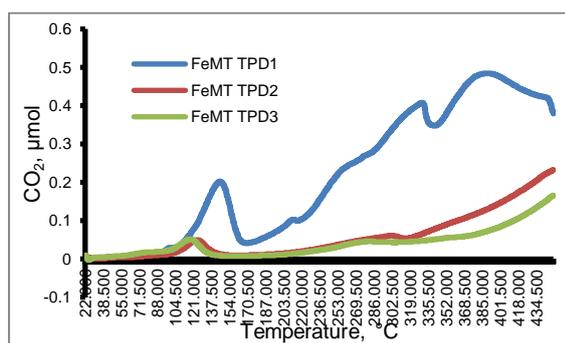


Fig. 6. TPD diagrams of CO₂ – temperature relation for the three samples of FeMT. CO₂: purge debit: 14 ml/min; TPD debit: 6 ml/min; Temperature domain: 23 ÷ 450°C.

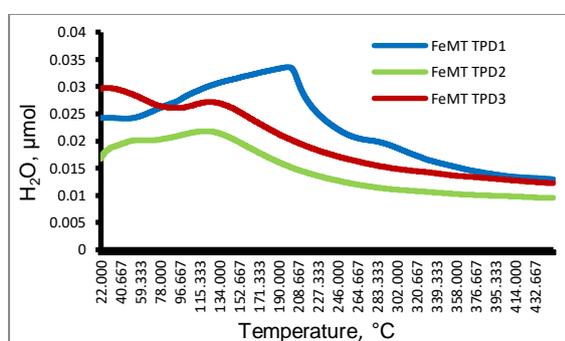


Fig. 7. TPD diagrams of H₂O – temperature relation for the three samples of FeMT. CO₂: purge debit: 14 ml/min; TPD debit: 6 ml/min; Temperature domain: 23 ÷ 450°C.

Table 1.
CRC and WRC values for the studied catalysts

Nr. of sample	CRC, [μmol/g]	WRC, [μmol/g]
NaMT TPD1	3821±5	111±5
FeMT TPD1	1109±5	116±5
BentA TPD1	2697±5	161±5
BentB TPD1	2081±5	119±5
AAB1 TPD1	2554±5	102±5
AAB4 TPD1	1976±5	97±5
AAB8 TPD1	2422±5	84±5
AAB15 TPD1	2080±5	70±5
AAB24 TPD1	2415±5	73±5

4. Conclusions

The results of this research are of great importance as they provide compelling evidence that natural materials such as clays can be used to develop inexpensive

water decontamination technologies. This is all the more interesting taking into account the wide availability of such materials, their ease of handling and modification, the non-use of solvents and other polluting chemicals, and especially the high chemical stability of bisphenol A, opens promising prospects for the treatment of water, especially that related to human health such as those used or discharged by the food and pharmaceutical industries and in domestic waste.

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