

Regeneration of a solid waste from an agri-food industry

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Abstract

The refining process of crude edible oil is based on four main operations: degumming, neutralization, bleaching and deodorization. The most critical and important step is bleaching, as it helps to improve the appearance, odor, taste and stability of the final products. During this step, the oil is put in contact with clay, called bleaching earth. This material has a large capacity to adsorb undesirable elements such as pigments (α -chlorophyll and β -carotene) and other residues (free fatty acids, phosphatides, soap residues and traces of heavy metals) that can be present in the crude oil. After having been used for the oil treatment, the bleaching earth loses its adsorption capacities and becomes a waste called spent bleaching earth (SBE). These solid waste containing up to 40% (w/w) of oil associated with other impurities, are generally disposed off in a landfill near the factory. As they are not treated, they may cause several management, storage and environmental problems, beside the unpleasant odors that can be produced. These environmental problems made the search for an alternative way to the landfill, a crucial matter. The main objective of this study was to contribute to reduce the pollution risk generated by these industrial wastes. The regeneration method used was based on a heat treatment of the SBE. The material obtained was a mixture of clay and coal and was then characterized by several techniques, namely: N_2 isotherm at 77K, FTIR and XRD. Its adsorption performance was estimated through kinetic adsorption using a basic dye. In order to enhance the results, its adsorption capacities were then compared with those found in virgin bleaching earth (VBE) and in L27 activated carbon (purchased from PICA JACOBI).

Keywords: Edible oil, Heat treatment, Regeneration, Reuse, Solid waste.

I. Introduction

Just after independence, Algeria had known important developments concerning the economy and the population demography which led to an accelerated urbanization and a non controlled industrial expansion, hence major consequences on the environment.

In fact the country is still facing huge problems related to the industry and to the protection of the environment, particularly due solid wastes which may be damaging for human health and the environment. The management of these industrial wastes is not well developed from the technical and organizational points of view and to date, the method used for the disposal of these industrial waste remains the landfills, because of its low cost

compared to other fields. This process is only valid in the cases of non-hazardous industrial wastes, known as ordinary industrial or household wastes. However in most cases industrial wastes are classified as hazardous requiring several safety measures to be taken and/or pretreatments before being discharged in landfills.

The local agri-food industry, and more specifically the edible oil refineries generate more than 8000 tons per year of spent bleaching earth (SBE) as wastes without undergoing any treatment [1-3]. According to the European Waste Catalogue, the spent bleaching earth is classified as hazardous waste to which is affiliated the code 07 06 10* (the asterisk indicates the waste hazard). Untreated SBE cannot be land filled due to its high organic content, which exceeds the limit of 6% of the waste acceptance

criteria for hazardous waste landfills under the European Union Landfill Directive [4]. Over time, the disposal of such wastes may be a source of many ecological and environmental problems and pollution which concerns soil, water and air. Indeed, this clay waste is loaded with impurities, dyes and a very large amount of oil entrained during the various refining stages (degumming, neutralization, bleaching and deodorization) which may be released to the environment. Thus, these spent bleaching earths not only show a risk of fire (spontaneous combustion), but also represent a potential source of water contamination and generating of unpleasant odors. Given these different environmental problems caused by discarding spent bleaching earths, the search of an alternative method to landfill is primordial and this is the purpose of this study.

II. Experimental

II.1 Materials

The spent bleaching earth (SBE) used in this study was provided by the unit of edible oil refining, unit of COGB-Label of Bejaia (Algeria). The virgin bleaching earth (VBE) is naturally active clay composed of mixed-layer of kerolite/stévensite from SEPIOGEL (Spain) company. The major chemical components of this material are as follows: 53.5 % SiO₂, 30.5 % MgO, 4 % Al₂O₃, 1 % K₂O, 0.7 % CaO, 1.5 % Fe₂O₃, and 0.3 % Na₂O. The activated carbon (AC) used was a granular activated carbon called L27, because of its high adsorption capacity with respect to organic micro pollutants [5]. The basic dye used as adsorbate in the present study was methylene blue (C₁₆H₁₈ClN₃S, MW = 319.8 g mol⁻¹, λ_{max} = 665 nm).

II.2 SBE treatment

The heat treatment of the SBE was carried out in a tubular furnace of type CARBOLITE under controlled atmosphere (Argon) set at 500 °C. This oven (Fig. 1) was equipped with heating elements (wound resistive wires) arranged around the working tube ensuring a high thermal uniformity (oven called tri-zone). The sample to be treated was put in one boat then introduced into the working tube in quartz. Ends of this tube were then plugged by adequate corks allowing the oven to be hermetic. The amount of the obtained material after carbonization was washed repeatedly with distilled water then dried and preserved. The final material was named RSBE.



Figure 1. The tubular furnace

II.3 Materials characterization

The DRX spectra of VBE, SBE and RSBE were obtained with monochromatic CuKα radiation using an X Pert Pro Panalytical diffractometer. The FTIR spectra of different samples (lozenge of KBr 1%) were carried out with Nicolet 6700 spectrometer, in the range 4000–400 cm⁻¹. The porous texture of the RSBE and VBE was characterized by nitrogen gas adsorption at 77 K, by using ASAP 2020, Micromeritics apparatus.

II.4 Kinetic study

The adsorption performance of the regenerated material can be estimated through the adsorption kinetics. The kinetic study was carried out at room temperature in a batch process. For each experiment, 50 mL of the methylene blue solution with concentration of 250 mg L⁻¹ were continuously stirred with 50 mg of the adsorbent during different time intervals (5-360 min). The suspensions were then centrifuged and the basic dye concentrations in the supernatant were measured with UV-visible spectrophotometer (UV-Vis Uvikon XS Bio-tek instruments) at 665 nm wavelength.

The amount of adsorbed dye per unit mass of adsorbent at time t , q_t (mg g⁻¹), was then determined by the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

Where C_0 and C_t (mg L⁻¹) are the initial concentration and liquid phase concentration of the basic dye solution at time t (min), respectively, V (L) is the volume of aqueous solution containing basic dye, and m (g) is the mass of adsorbent used.

III. Results and discussion

The FTIR spectrum of different samples VBE, SBE and RSBE (Fig. 2) show the disappearance of the edible oil characteristic bands in the spent bleaching earth after the heat treatment at 500 °C. These bands are those corresponding to C-H stretching at 2925 and 2850 cm⁻¹.

2854 cm^{-1} and the ester carbonyl vibration at 1736 cm^{-1} [3, 6]. The departure of these compounds did not reveal any notable changes in the structure of these materials. This result was confirmed by the X-ray diffraction (Fig. 3) which showed that the crystalline structure of the different samples was clearly not affected by the heat treatment.

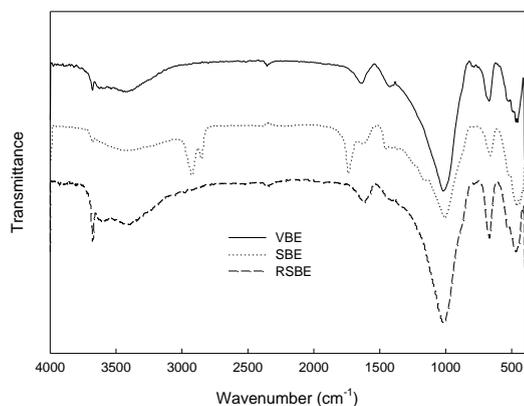


Figure 2. FTIR spectra of VBE, SBE and RSBE

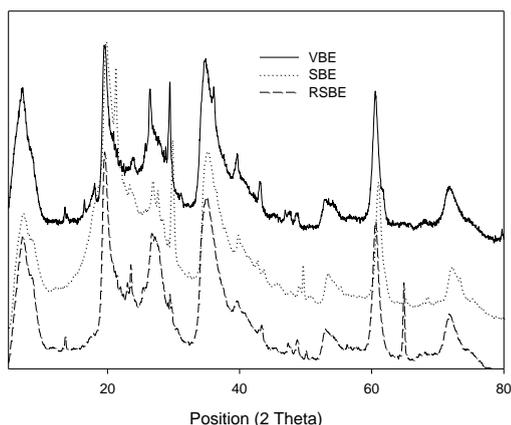


Figure 3. X-ray diffraction powder of VBE, SBE and RSBE

Tab. 1 enumerates the textural characteristics of VBE and regenerated material. Referring to the obtained results, we notice that the regenerated material has less textural properties compared to those of the VBE. This can be explained by residues remaining in the pores that cannot be completely removed by thermal regeneration [6]. Besides, the nitrogen adsorption isotherms at 77 K and the micropores size distribution curves of VBE and RSBE were determined.

Table 1. The textural characteristics of VBE and regenerated material

	V_{PT}	V_{mic}	S_{BET}	S_{ext}	S_{mic}
	($\text{cm}^3 \text{g}^{-1}$)	($\text{cm}^3 \text{g}^{-1}$)	($\text{m}^2 \text{g}^{-1}$)	($\text{m}^2 \text{g}^{-1}$)	($\text{m}^2 \text{g}^{-1}$)
VBE	0.25	0.05	207	139	49
RSBE	0.18	0.03	123	119	43

The curves of nitrogen adsorption isotherms of VBE and RSBE are presented on Fig. 4. The shape of these isotherms are similar and connected to type IV according to the Brunauer, Demming, Demming and Teller (BDDT) classification with the hysteresis corresponding to type H_3 of the International Union of Pure and Applied Chemistry classification (IUPAC) [7]. It is well known that the type IV isotherms are characteristic of mesoporous materials. The shape of hysteresis characterizes the shape of the pores and the H_3 type indicates that the two materials have slit-shaped pores [7]. What can appear at materials composed of plate-like particles or of a layer structure that is typical of clay structures. Also such type of hysteresis is the sign of a particle agglomeration forming the slits with sizes or forms non-uniform [8].

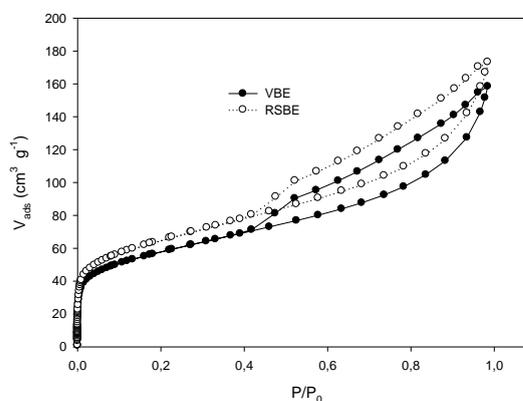


Figure 4. Isotherms for the adsorption and desorption of nitrogen at 77K on the VBE and RSBE samples.

The distribution of the micropore sizes obtained by DFT method is presented on Fig. 5. The obtained results show that the micropores of all samples had a heterogeneous distribution with a major peak at about 13 Å. It is clear that the thermal regeneration allowed some restoration of micropores with a similar distribution to that of VBE.

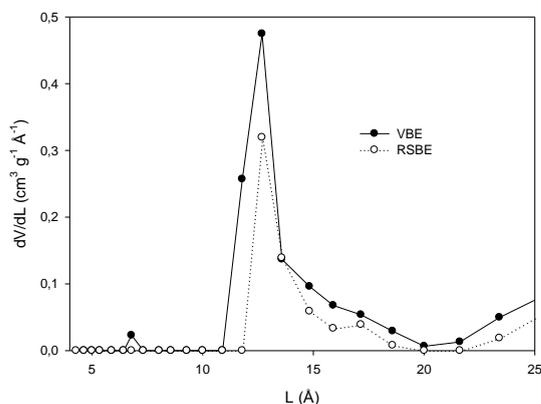


Figure 5. Micropore size distribution of samples (DFT method)

After the regeneration of the material (RSBE) and its characterization, its adsorption capacities were tested in the removal of the methylene blue present in aqueous solution, by referring to the virgin bleaching earth and the activated carbon L27. The curves of adsorption kinetics were obtained by plotting the adsorption capacity q_t (mg g^{-1}) according to time (min). The evolution of the adsorption capacity as a function of time for the both adsorbents studied is shown in Fig. 6 where it can be seen that the adsorption kinetics of all adsorbents took the same forms characterized by a strong increase of the adsorption of the basic dye in the first minutes of contact dye-adsorbent, followed by a slow increase until reaching equilibrium. The time necessary to reach this equilibrium was less than 30 min for VBE and RSBE and it was about 240 min for AC. The fast adsorption kinetic observed at the beginning of the process, can be interpreted by the fact that at this moment the number of active sites available on the surface of the material was important. After a time spent by the material in the dye solution, the remaining vacant sites became difficult to be occupied due to their localization inside the pores or the micropores of material (see Tab. 1) and as well as to the existence of the repulsion forces between the molecules of the dye adsorbed by material and those which were in solution [9]. By comparing the amounts of basic dye adsorbed at equilibrium by the different adsorbents, it is found that VBE fixed more dye than the regenerated material and the Activated carbon and that regenerated spent bleaching earth gave better results than those with commercial activated carbon despite its large specific surface area ($1575 \text{ m}^2 \text{ g}^{-1}$).

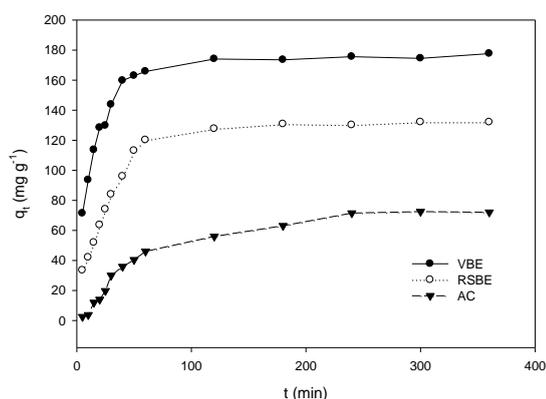


Figure 6. Evolution of the adsorption capacity according to time for VBE, RSBE and AC

IV. Conclusion

The obtained results showed that the regeneration of spent bleaching earth by heat treatment was possible.

The resulting material RSBE (a mixture of clay and carbon) had significant adsorption capacities. Indeed, the elimination tests of a basic dye, such as methylene blue, by the regenerated spent bleaching earth gave better results than those with commercial activated carbon.

List of symbols and abbreviations

C_0	Initial concentration of basic dye
C_t (mg L^{-1})	Liquid phase concentration of the basic dye solution at time t
L (\AA)	Width of micropores
λ_{max} (nm)	Maximum wavelength
m (g)	Mass of adsorbent
MW (g mol^{-1})	Molecular weight
P (Pa)	Pression
q_t (mg g^{-1})	Amount of basic dye adsorbed at time t
S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	Specific surface area calculated by BET method
S_{ext} ($\text{m}^2 \text{ g}^{-1}$)	External surface area
S_{mic} ($\text{m}^2 \text{ g}^{-1}$)	Micropores area
t (min)	Time
V (L)	Solution volume
V_{ads} ($\text{cm}^3 \text{ g}^{-1}$)	Volume of adsorbed nitrogen
V_{mic} ($\text{cm}^3 \text{ g}^{-1}$)	Micropores volume
V_{PT} ($\text{cm}^3 \text{ g}^{-1}$)	Total porous volume
<i>RSBE</i>	Regenerated Spent Bleaching Earth
<i>SBE</i>	Spent Bleaching Earth
<i>VBE</i>	Virgin Bleaching Earth

References

- [1] A. Boukerroui and M.S. Ouali, Regeneration of a spent bleaching earth and its reuse in the refining of an edible oil, J. Chem. Technol. Biotechnol., 75 (2000) 773-776.

- [2] M. Mana, M.S. Ouali and L.C. De Menorval, Removal of basic dyes from aqueous solutions with a treated spent bleaching earth, *J. Colloid Interface Sci.*, 307 (2007) 9-16.
- [3] C. Meziti and A. Boukerroui, Regeneration of a solid waste from an edible oil refinery, *Ceram. Int.*, 37 (2011) 1953-1957.
- [4] A.F. Rehab, N.A. Mostafa, S.M. Mohamed and A. Wael, Recovery of oil and free fatty acids from spent bleaching earth using sub-critical water technology supported with kinetic and thermodynamic study, *Adv. Biosci. Biotechnol.* 5 (2014) 261-272.
- [5] T.F. De Oliveira, O. Chedeville, B. Cagnon, H. Fauduet, Degradation kinetics of DEP in water by ozone/activated carbon process: influence of pH, *Desalination* 269 (2010) 271- 275.
- [6] W.T. Tsai, H.P. Chen, M.F. Hsieh, H.F. Sun and S.F. Chien, Regeneration of spent bleaching earth by pyrolysis in a rotary furnace, *J. Anal. Appl. Pyrolysis.*, 63 (2002) 157-170.
- [7] A. Lecloux, Exploitation des isothermes d'adsorption et de désorption d'azote pour l'étude de la texture des solides poreux, *Mémoire Société Royale des Sciences de Liège*, 6ème série, tome I, Fasc 4 (1971)169–209.
- [8] W.T. Tsai, H.P. Chen, W.Y. Hsien, C.W. Lai and M.S. Lee, Thermochemical regeneration of bleaching earth waste with zinc chloride, *Resour. Conserv. Recycl.*, 39 (2003) 65 - 77.
- [9] C. Meziti and A. Boukerroui, Reuse of Solid Waste in Adsorption of the Textile Dye, *Phys. Procedia.*, 55 (2014) 173 - 178.