

Removal of methylene blue dye from water by a spent bleaching earth biosorbent

Ali Belhaine, Mouffok Redouane Ghezzer, Fatiha Abdelmalek, Kamel Tayebi, Abdelhamid Ghomari and Ahmed Addou

ABSTRACT

This work is about the valorization of spent bleaching earth (SBE) at low cost from the AFIA oil refinery in Algeria's western region. The biowaste has been burned to eliminate the oil traces, then it has been valorized in two ways: (i) chemically, using phosphoric acid to obtain SBEC and (ii) thermally at 750 °C to create SBEH. The obtained materials were used for the first time as biosorbents in the wastewater treatment field. The three biomaterials show very interesting adsorption properties, with specific surfaces of 194.2, 784.6 and 888.5 m² g⁻¹ for SBE, SBEC and SBEH, respectively. The analysis has revealed that the obtained materials are alumino-silicates. The three biowastes have been used to remove methylene blue dye from water. The dye was totally eliminated by a physisorption mechanism in the presence of 1 g L⁻¹ of each biowaste after 8, 10, 20 min of contact time. The highest correlation coefficient ($R^2 = 0.99$) was related to the Langmuir isotherm, indicating a good fit with this model, and explaining the biosorption as a monolayer process. According to this model, the adsorption capacities were 123.3, 185.2 and 188.7 mg g⁻¹ for SBE, SBEH and SBEC, respectively. This study shows that SBE can be used as an alternative to commercial adsorbents for dye removal from water.

Key words | adsorption, alumino-silicate, methylene blue, oil refinery, spent bleaching earth

Ali Belhaine

Mouffok Redouane Ghezzer (corresponding author)

Fatiha Abdelmalek

Ahmed Addou

Laboratoire des Sciences et Techniques de l'Environnement et de la Valorisation (STEVA), Université de Mostaganem, BP 188, Mostaganem 27000, Algeria

E-mail: m.ghezzer@univ-mosta.dz; redouane.ghezzer@univ-mosta.dz; ghezzer_redouane@yahoo.fr

Kamel Tayebi

Laboratoire de Science et Genie des Matériaux, USTHB, Alger, Algeria

Abdelhamid Ghomari

Laboratoire Structure, Elaboration et Application des Matériaux Moléculaires, Université de Mostaganem, Mostaganem 27000, Algeria

INTRODUCTION

The fat industry generates important quantities of spent bleaching earth (SBE) during refining operations (Krzyśko-Lupicka *et al.* 2014). In Algeria, edible oil refineries produce about 8,000 tonnes per year (Abdel Fattah *et al.* 2014), especially the AFIA plant, whose activity is the refining and conditioning of table oil.

The adsorbents used for refining the oil are clay minerals, activated or not, and present in the forms of alkaline, alkaline-earth, synthetic silicates, alumino-silicates, metallic silicate oxides and mixed metallic silicate oxides (Prokopov & Mechenov 2013). By appropriate treatments, the SBE can be given adsorption properties and can be utilized in the treatment of wastewaters (Mana *et al.* 2011).

Methylene blue (MB) is known as a dye of the thiazine type, and it is commonly used as a representative of the common organic dyes that contaminate textile effluents. It reduces light penetration and photosynthesis, and it damages the aesthetic nature of the water surface (Prokopov & Mechenov 2013). It is largely used in the

textile, plastic, paper and leather industries, and for coloring cosmetic products. It may be harmful to flora and the fauna, and it has been reported to be carcinogenic and mutagenic (Prokopov & Mechenov 2013; Sadaf *et al.* 2015).

Among the many treatment processes that are applied to effluents contaminated by dyes, such as biodegradation, advanced oxidation processes, reverse osmosis, ion exchange, precipitation, adsorption, flocculation, filtration, etc. (Sadaf *et al.* 2014), adsorption is the most utilized method to remove MB dye from wastewaters (Prokopov & Mechenov 2013). It is a reliable and good alternative because of its simplicity, its great efficiency, and the availability of a large range of adsorbents whether natural or synthetic (Bhatti & Nausheen 2015).

The main objective of our work is to valorize the SBE biomaterial rejected by the AFIA factory. In our study, we have used the SBE as a biosorbent either treated chemically or thermally to remove MB dye from water.

MATERIAL AND METHODS

Preparation of adsorbents

The valorization of SBE as an adsorbent requires the elimination of oil. The first operation consisted of eliminating the oil and any large particles by burning and sieving ($>45\ \mu\text{m}$). The obtained material was subjected to two different treatments: a chemical treatment by impregnation in a solution of H_3PO_4 (30% w/w) over 24 h (Jagtoyen *et al.* 1992). The material obtained is called SBEC. The other treatment consisted of heating the SBE in a furnace at $750\ ^\circ\text{C}$ for 8 h at a heating rate of $5\ ^\circ\text{C}/\text{min}$ to obtain a material called SBEH (Ahmadpour & Do 1996).

Reagents

All reagents used are of analytical grade and were purchased from Merck (Germany). MB dye solutions were prepared by dissolving an appropriate quantity of MB (a cationic dye) of chemical formula $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ (MW = $319.87\ \text{g mol}^{-1}$ and purity = 95%) in distilled water.

Characterizations

The sample compositions were confirmed by energy dispersive X-ray spectroscopy analysis. The X-ray diffraction (XRD) patterns were collected on a Panalytical X'Pert Pro diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.540598\ \text{\AA}$). The scan range was kept the same for all samples ($2\theta = 20^\circ - 100^\circ$) using a step size of 0.01° with a sample time of 10 s.

For recording IR spectra, samples were prepared by mixing a small quantity with KBr. The mixed sample powder was pressed in a cylindrical disc at $10\ \text{tons}/\text{cm}^2$ by a hydraulic press. The IR measurements of the prepared samples were recorded in a range from $400\ \text{cm}^{-1}$ up to $4,000\ \text{cm}^{-1}$ using a Fourier transform infrared spectrophotometer (Thermo Scientific Nicolet 380 FTIR Spectrometer).

The specific surface areas were measured and calculated according to the Brunauer–Emmett–Teller (BET) method using Micromeritics ASAP2020 with N_2 as an adsorbate at 77 K.

The micropore volume (V_{micro}), micropore area (S_{micro}) and external surface area (S_{ext}) were calculated by the t-plot method. The total pore volume (V_{total}) was estimated from the volume of N_2 adsorbed at a relative pressure $P/P_0 = 0.96$.

Batch adsorption experiments

The adsorption studies were carried out in a 25 mL Erlenmeyer flask. The MB solution was prepared with deionized water. The adsorption of MB dye by SBE was investigated for an initial dye concentration range of $100\text{--}400\ \text{mg L}^{-1}$ at different adsorbent doses (1, 2 and $3\ \text{g L}^{-1}$).

The concentrations of dye and the dose of adsorbent were chosen based on earlier studies with a similar system (Tsai & Chen 2010). The flasks were stirred at 100 rpm using a mechanical stirrer. The temperature of the dye solution during the adsorption studies was maintained at $25\ ^\circ\text{C}$. The samples were withdrawn at regular intervals of up to 2 h and were filtered using a mixed cellulose ester membrane with a pore size of $0.45\ \mu\text{m}$. The dye concentration in the filtered solution was measured using a UV/Visible spectrophotometer (OPTIZEN 2020 double beam) at a wavelength of 665 nm. The amount of adsorption at equilibrium, q_e (mg g^{-1}) was determined by the following equation:

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

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentrations of MB, respectively, V is the volume of the solution (L) and m is the mass of adsorbent used (g).

RESULTS AND DISCUSSION

XRD analysis

The XRD spectra of the three samples are shown in Figure 1. The indexes show that they are mineral compounds consisting of montmorillonite (M), quartz (Q), calcite (C), illite (I), dolomite (D) (Zhang *et al.* 2015), and certain unidentified compounds. The diffractogram shows large peaks, having very bad resolution, indicating bad crystallinity for SBE. However, the narrow form of the peaks of SBEC and SBEH indicate a better crystallinity due to the chemical and thermal treatment.

The results of the material's mineralogical composition suggests that it is a bentonite utilized by the factory for removing color from their oils. Indeed, it is known that this type of earth is widely used as a decoloring agent for food oils (Pollard *et al.* 1993).

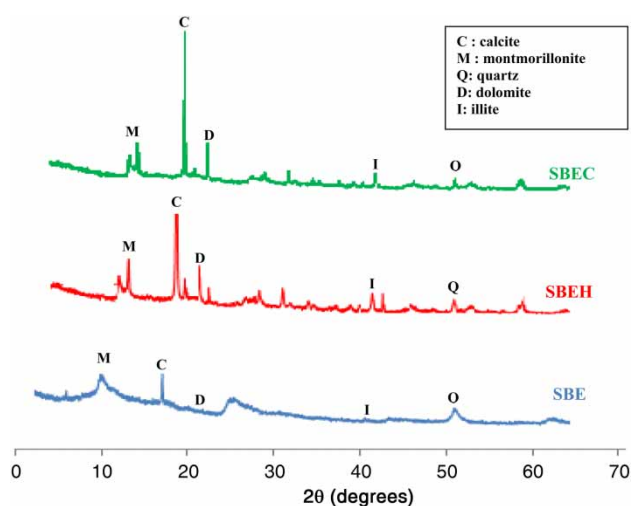


Figure 1 | XRD analysis of the three materials (SBE, SBEH and SBEC).

Structural and textural properties

Analysis by the BET method

The isotherms of adsorption-desorption using N_2 according to the BET method for the three materials (SBE, SBEH and SBEC) are shown in Figure 2(a). They show a structural synergy between the micropores and the mesopores. The distribution of pore sizes calculated by the method of Barrett, Joyner and Halenda (BJH) (Tong *et al.* 1992) for the three samples is shown in Figure 2(b).

The measurements obtained for the specific surface, the volume of the pores, the volume of micropores and mesopores are provided in Table 1. The results show that the specific surface varies from 194.2 to $784.6 \text{ m}^2 \text{ g}^{-1}$ for thermally treated waste and to $888.5 \text{ m}^2 \text{ g}^{-1}$ for chemically treated waste. So, these two treatments have led to an important increase in the specific surface. This result encourages the use of these materials as biosorbents to remove refractory organic compounds such as dyes.

The results show also a significant increase in the volume of porosity in its two forms. The general volume of pores has been multiplied by 3.2 and 3.5 for thermal and chemical treatments, respectively, consequently leading to a practical doubling of the micropores' volume and a quadruple effect on the mesopores' volume. The existing impurities in the pores reduce their volumes, but an acid attack or thermal treatment can remove these impurities from the pores by abrasion. Changes noticed in the SBE structure are probably caused by the following:

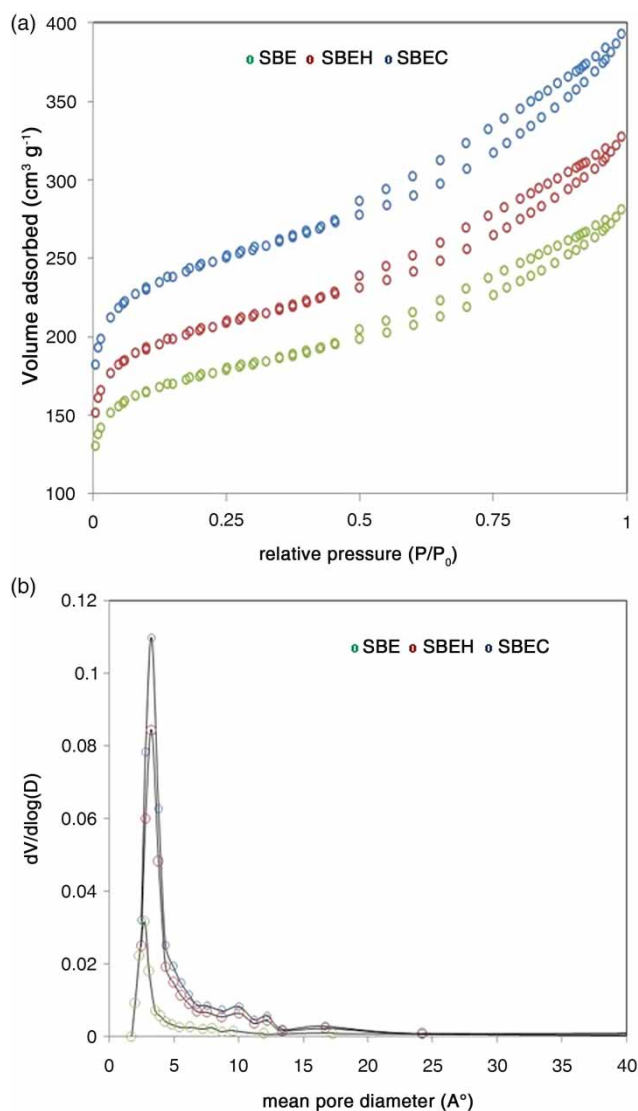


Figure 2 | (a) BET analysis- N_2 adsorption-desorption isotherms of the samples; (b) pore size distributions and cumulative pore volumes of the samples.

Table 1 | Surface area and pore volume data of samples

Adsorbent	BET surface area ($\text{m}^2 \text{ g}^{-1}$)	Total pore volume ($\text{cm}^3 \text{ g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{ g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{ g}^{-1}$)
SBE	194.2	0.323	0.111	0.212
SBEH	784.6	1.051	0.247	0.857
SBEC	888.5	1.131	0.271	0.822

- (i) The phosphoric acid, being a strong acid, tends to liberate protons, which diffuse via the surface of the biosorbent causing the cleaning of the pores.

(ii) The heat flux behaving as a strong oxidant of the organic matter present on the surface and the interstitial volume of SBE. This will allow the liberation of more space at the surface, and will cause the desorption of residual oil from the pores. This action remains similar to the oxidizing effect of H_3PO_4 , but is very limited by the heterogeneity of the thermal treatment with regard to a dispersed medium like the SBE biosorbent (Wu *et al.* 2015).

FTIR analysis

The infrared spectra of samples of crude and treated wastes are shown in Figure 3. The sample of crude waste shows a fine band at $3,620\text{ cm}^{-1}$ attributed to stretching vibrations of hydroxide groups (OH) of the constituent water. This band tends to disappear when the chemical and thermal treatments are applied, eliminating the non-associated OH groups. The strong and large band in the range from $3,400$ to $3,200\text{ cm}^{-1}$, whose maximum is situated at $3,420\text{ cm}^{-1}$, is characteristic of the stretching vibrations of OH groups of Al-OH bonds. The applied treatments were not able to remove the concerned groups. Indeed, whatever the type of the oxidation, thermal or chemical, it more easily degrades the O-H bonds, which are physical bonds or van der waals type, and has little effect on the stronger chemical bond, as is observed in this case.

The band at $1,620\text{ cm}^{-1}$ is attributed to H-OH deformation vibrations due to the adsorbed water molecules (Mohammed *et al.* 2014). A weaker intensity band at

$1,410\text{ cm}^{-1}$, characteristic of the stretching vibration modes of C-O bonds, is attributed to the asymmetrical stretching vibration modes of carbonate.

This band, which decreases with the treatment, shows that the disappearance of organic matter and/or carbonates into CO_2 by acidification and thermally is more intense in SBEC material. The intense band located between 950 – $1,050\text{ cm}^{-1}$ and centered at $1,000\text{ cm}^{-1}$ corresponds to the valence vibrations Si-O (Mohammed *et al.* 2014) in SBE. The treatments applied to the latter have little effect on the presence of organic compounds since we find the same bands with important intensities in the FTIR spectra of the treated samples.

The band at 987 cm^{-1} is attributed to the Al-OH vibrations, the one at 877 cm^{-1} corresponds to the deformation of Al-Mg-OH or Al-Fe-OH, and the other at 797 cm^{-1} is attributed to the vibrations of quartz. The band at 500 cm^{-1} is attributed to the deformation vibrations of Si-O-Al (Lerot & Low 1976; Mohammed *et al.* 2014).

MB adsorption

Contact time effect-adsorption kinetics

The effects of contact time on the adsorption of MB into the three samples are shown in Figure 4(a). For the MB solution with an initial concentration of 100 mg L^{-1} and a natural pH value of 6.1, a rapid elimination of dye molecule, is noticed for all samples: the contact times to achieve equilibrium were 5, 10 and 20 min for SBE, SBEH and SBEC, respectively.

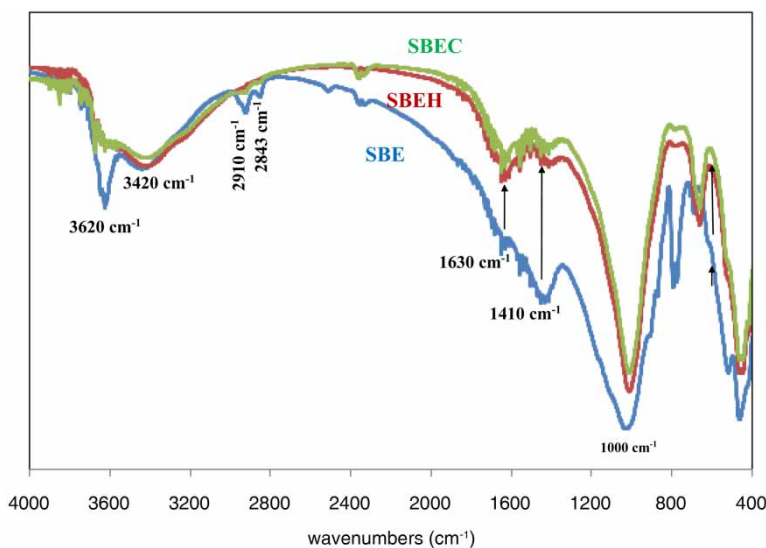


Figure 3 | FTIR spectra of the three materials (SBE, SBEH and SBEC).

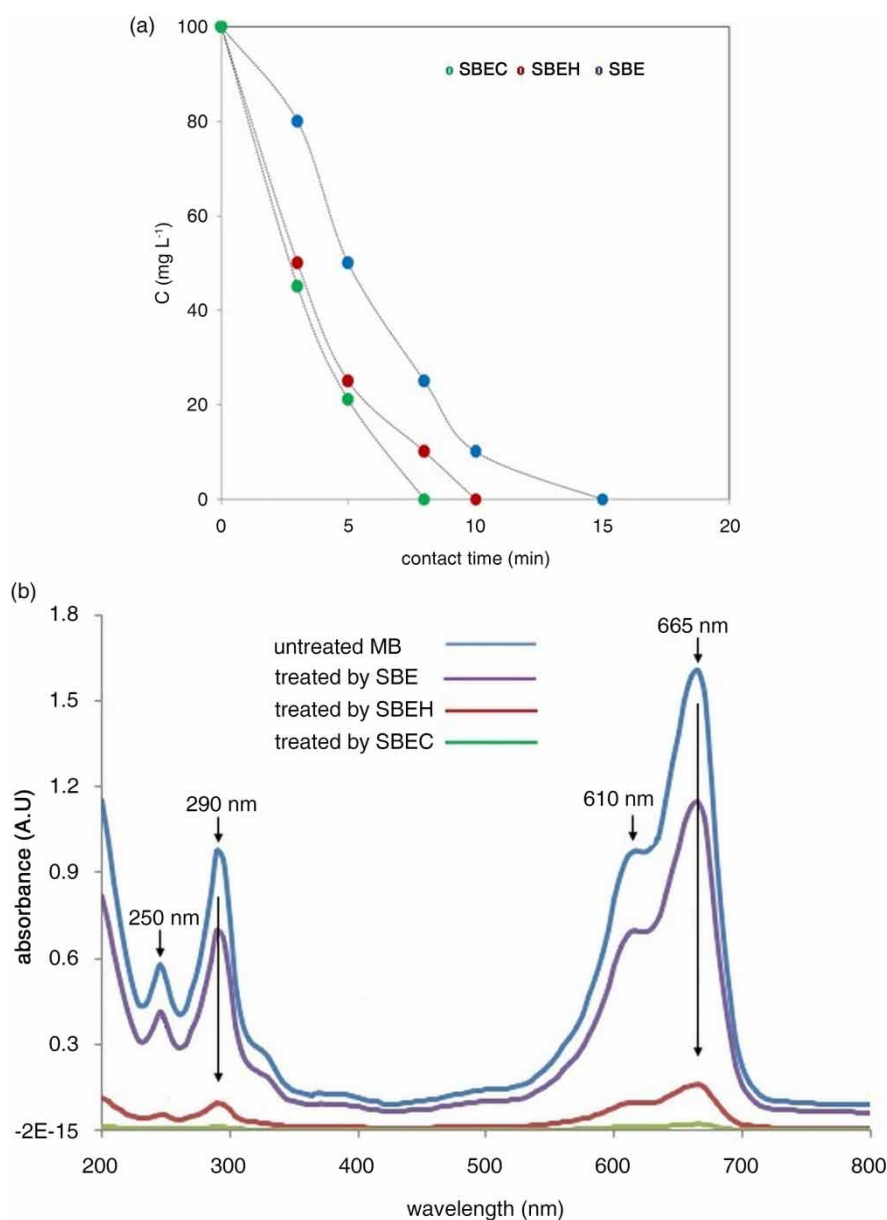


Figure 4 | (a) MB adsorption contact time, (b) UV/vis spectra of MB dye treated during 5 min by SBE, SBEH and SBEC.

Figure 4(b) shows the UV/visible spectra of MB dye (100 mg L^{-1}) in aqueous solution with three separated earths (1 g L^{-1}) at a contact time of 5 min. The crude MB sample consists of three absorption bands, one at 665 nm with a shoulder at 610 nm, corresponding to the thiazine chromophore group, and two others at 250 and 290 nm corresponding to groups of ammonium dimethyl and benzene cycles, respectively. A contact time of 5 min with the SBE led to a decrease in these characteristic bands at rates of 29, 90 and 100% for SBE, SBEH and SBEC, respectively. This disappearance is attributed to

the adsorption of the MB colorant on the material's surface. The fact that no new band appears shows well that no chemical reaction takes place during the adsorption process. A physisorption mechanism seems suitable to eliminate the MB molecules by the three earths (Ayad & Abu Ahmed 2010).

This implies a strong electrostatic interaction between the negatively charged surface of the spent solid wastes and the cationic MB. Then, the adsorption increases very slowly with the extension of time. A similar tendency has been reported by other authors who have studied the

adsorption of MB dye by synthetic aluminosilicate materials (Wu et al. 2015; Zhang et al. 2015).

Adsorption isotherms

The adsorption isotherms are essential for the understanding of the adsorption mechanisms. Currently, two classical models are used to describe these isotherms, i.e., the Langmuir and Freundlich equations. The Langmuir model is based on the assumption that the adsorption occurs at local and homogeneous sites on the adsorbent (monolayer adsorption). The Langmuir equation can be described as follows (Langmuir 1916):

$$\frac{x}{m} = \frac{K b C_e}{1 + K C_e} \quad (2)$$

where C_e is the MB concentration at equilibrium (mg L^{-1}); q_e is the amount of MB adsorbed (mg g^{-1}) K is a constant and b is the maximal capacity of adsorption (mg g^{-1}).

The Freundlich model is expressed by the following expression (Freundlich 1906):

$$\frac{x}{m} = K_f C_e^{1/n} \quad (3)$$

where C_e is the MB concentration at equilibrium (mg L^{-1}); q_e is the amount of MB adsorbed (mg g^{-1}); K is a constant and $1/n$ is the adsorption intensity.

Figure 5 expresses the variation in the amount adsorbed per 1 gramme of material depending on the concentration of MB dye at the equilibrium. It is found that the amount of adsorbed dye increases with the concentration of the dye to reach a saturation level.

The mathematical adjustment of the two isotherms shows that the adsorption of MB follows the Langmuir model with high values of correlation coefficients (Table 2). The linearization of Equations (2) and (3) calculates the parameters that govern the two models. As was established by the structural analysis, the chemical treatment by phosphoric acid strongly increases the adsorption capacity from 123.3 to 188.7 mg g^{-1} ; according the following order of efficiency: SBEC > SBEH > SBE.

Indeed, the cleaning of the active sites of SBE by acid attack can explain the elimination of residual oil existing in the interlayer spaces, and contributes to the creation of additional sites, so promoting the adsorption of MB dye on the SBE material (Chang et al. 2015; Din et al. 2016).

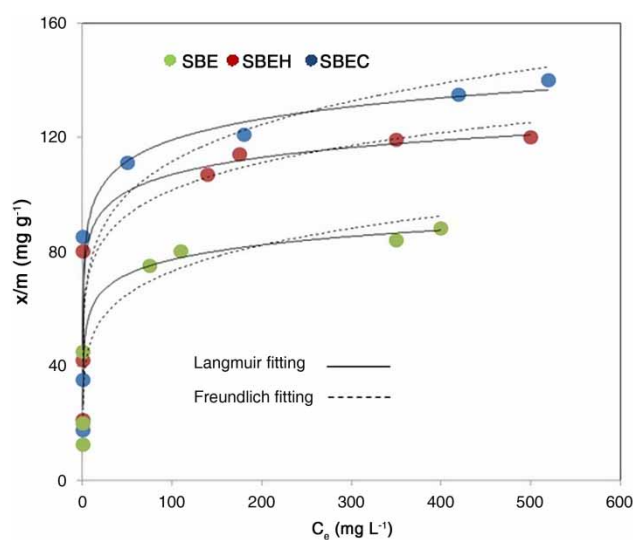


Figure 5 | Langmuir and Freundlich isotherms adsorption of MB dye in the presence of SBE, SBEH and SBEC.

Table 2 | Langmuir and Freundlich isotherm model constants and correlation coefficients

Adsorbent	Langmuir model			Freundlich model		
	b (mg g^{-1})	K (L mg^{-1})	R^2	K_f (L g^{-1})	n	R^2
SBE	123.3	0.010	0.99	1.34	3.36	0.436
SBEH	185.2	0.060	0.99	1.49	2.68	0.795
SBEC	188.7	0.013	0.99	1.11	10.25	0.803

The adsorption mechanism seems to depend on ionic/electrostatic interactions between the negative charge of the surface of the adsorbents and the positive charge of the MB dye molecule. Similar results were obtained by Tsai & Chen (2010) in the adsorption of malachite green dye by dead biomass *Chlorella*. This effect may only be marginal, occurring on the surface of adsorbents, the most important is the migration of MB molecules into the pores of the material.

The proposed mechanism would be: (i) migration of the dye molecule to the surface of the adsorbent through electrostatic force and (ii) infiltration into the pores, in particular the micropores. This mechanism can be valid in this case, since SBE contains fewer pores and a smaller specific surface. The modest adsorption of MB dye by SBE would be favored by the electrostatic force, and the organophilic characteristic of this material due to the presence of food oils. The improvement in the adsorption process by the other treated solid wastes is related to the simultaneous presence of the previously mentioned mechanisms and the increase in the specific surfaces.

CONCLUSION

The present study suggests that the SBE of the AFIA factory can be used as a non-conventional adsorbent for the removal of MB from water. This dye may be present in a real textile wastewater. SBE was chemically and thermally treated to obtain SBEC and SBEH modified materials, respectively.

The analysis by DRX, BET and FTIR enabled an understanding of the structural properties of the materials and identification of the type of the clay, which contained montmorillonite, quartz, calcite, illite and dolomite. The adsorption mechanism follows the Langmuirian physisorption according the following efficiency sequence: SBEC>SBEH>SBE.

Other valorization methods are under study for better management of the AFIA SBE biowaste.

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