



Waste of pine seeds as bio-removal agent for methylene blue from aqueous solution: regeneration and single-stage batch design

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ABSTRACT

The wastes of pine seeds after juice extraction were tested to remove the methylene blue from artificially polluted solution. The effect of heat treatment at various temperatures (100°C, 200°C, 300°C, 400°C, and 500°C) of these wastes, were investigated. These materials were characterized using Fourier transform infrared spectroscopy, X-ray diffraction, energy dispersive X-ray spectroscopy, scanning electron microscopy, and thermogravimetric analysis (TGA). The results indicated that their wastes were mainly composed of carbon, with a non-crystalline phase. Poly-functional groups on the surface were detected and were essential for the elimination of methylene blue dyes. The maximum removal capacity was estimated using the Langmuir model, and it was estimated to 110 mg/g at higher pH of MB solution of 11. The removal process was considered as endothermic process, and it occurred spontaneously. The regeneration process showed that the removal property was achieved after four cycles, with a decrease of removal percentage of 15%. A single-stage batch absorber design for MB removal has been suggested based on the Langmuir isotherm model equation.

Keywords: Pine seeds; Biosorbent wastes; Removal; Methylene blue; Mass balance; Single-stage batch design

1. Introduction

The Aleppo pine is the mainly copious *Pinus* species in Tunisia, [1]. This species (*P. halepensis*) is important in Tunisia because its cones offer the only appropriate seed source used for many human and forestry function [2,3]. The Aleppo pine seeds are traditionally used all over Tunisia, for the preparation of sweet pudding of ground pine seeds, known as *Assida-zgougou*.

During the grinding with a hand-operated mill, the oil was produced as a second phase; however, to prepare

the *Assida*, the grinded *zgougou* was soaked in water for few hours to extract the juice, and then separated through a fine cloth to extract the juice. The remaining solid was thrown away, and one could imagine the huge amount of the produced waste if it is counted by all the houses in the country. This waste was not explored in any means, and it reached the land field as a part of the waste discharge.

The scarcity of fresh water has been considered as a major concern to all the countries. The economic prosperity and the agricultural production expansion are requesting

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continuous demand of water. To minimize the dependence on this water resource, the use of recycled water is proposed as an alternative way. Among the industries that consumed an important amount of water, is the textile industry [4], and the resulting wastewater is required to be treated before it recycle or drained in the water streams. Several chemical, physical, and biological procedures have been proposed for the removal of dyes from contaminated water, such as anaerobic and aerobic microbial degradation, chemical precipitation, membrane separation, ion exchange, flocculation, electrochemical treatment, adsorption, and reverse osmosis [5]. Although the availability of mentioned methods, the adsorption process remains as the most promising method used in wastewater treatment, and could be considered as effective and attractive process, due to its ease of simplicity, operational procedure and suitability to treat concentrated dye wastes [6,7].

The wide-range accessibility of different adsorbents and in the most of cases, their natural availability with very low price, makes this technique more, and more attractive. Among these adsorbents, agricultural wastes and by products, known as biomass adsorbents were proposed. Many review papers were reported in this regard [8,9]. For example, the agricultural waste peels have been considered as an ecological burden for the society, however, they were the focus of many studies to explore them as renewable, low cost, and sustainable adsorbents for water treatment applications [10].

The methylene blue dye has been chosen because it was repeatedly used in the textile manufacturing and biological tissue staining [11]. In addition, MB has various harmful effects. The high concentration of this dye in contact with the eye can cause corneal injury in human beings. Doses in the range 500 mg can lead to anemia, dizziness, headache, abdominal pain, nausea, profuse sweating, and mental confusion, in addition is harmful to aquatic life, since its existence in water can rigorously decrease sunlight diffusion, affecting the production of nutrient by autotrophic aquatic organisms [12,13]. Although this type of pine seeds and its use in daily life in agricultural, food, and pharmaceutical domains are well-established. However, the application of the generated waste materials has not been explored. In this study, the usage of these materials was investigated in the treatment of polluted water, and was proposed as removal agent of methylene blue dye from artificially polluted solutions. The waste of pine seeds was characterized before its use, by different techniques, such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), and thermogravimetric analysis (TGA). The most relevant parameters for removal process were evaluated, such as initial concentration, waste pine dose, temperature, and pH of MB solution. In addition, thermodynamics and adsorption isotherm with the theoretical models were investigated. The gap between the theory of the isotherm model and its application is to propose an experimental framework and to design a batch reactor. In addition, the regeneration of selected waste materials during the removal process was also carried out using a friendly method as reported in our previous study [14].

2. Experimental part

2.1. Materials

The pine seeds were harvested in Siliana (Tunisia), and were bought from a local herbal dealer. The seeds were cleaned manually for removing any foreign matter, and then milled in a manual grinder. The aroma of the pine seeds was extracted during the preparation of Assida, as described in the introduction paragraph.

The methylene blue (MB) was purchased from Sigma-Aldrich, and used as obtained. The used MB has a chemical formula of $C_{16}H_{18}Cl_3S \times H_2O$ with molecular weight of 319.86 g/mol. Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) and $Co(NO_3)_2 \times 6H_2O$ were used without further treatment after purchase from Alfa Aesar (Binfield Berkshire, UK) (4.7% active oxygen).

2.2. Thermal treatment of waste pine

The fresh pine seeds are assigned as FPS. The resulting waste is assigned as SWP. The SWP was heat treated at different temperatures from 100°C to 500°C, in a Thermo-Fischer bench top muffle furnace (model Thermolyne 5.8 L D1) in air atmosphere for 2 h. The temperature values were deduced from the TGA study. The samples are assigned as following, that is, SWP (200), indicates that the SWP was heat treated at 200°C, before its use for removal process.

2.3. Removal of MB dye

The MB stock solutions (1,000 mg/L) and subsequent work solutions were prepared with deionized water from appropriate dilutions. The pHs of work solutions were adjusted using 0.1 mol/L of HCl and/or NaOH solutions.

All batch experiments were performed in laboratory scale suspending known masses of SWP or heat-treated samples into the MB work solutions, the suspension was stirred at 120 rpm in a water shaker path adjusted at 25°C for overnight. The supernatants were separated from the solids by centrifugation and analyzed using a UV/visible spectrophotometer. External calibration has been used to conclude the concentrations of the remaining MB analyte.

The percentage and the amount of removal of MB were calculated by Eqs. (1) and (2), where C_0 and C_e are the initial and final concentrations of MB in the working solution and supernatants from removal experiments, respectively.

$$q_e = (C_0 - C_e) \times \frac{V}{M} \quad (1)$$

$$R\% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

The removed MB q_e (mg/g) was calculated by Eq. (1), where C_e and C_0 are the equilibrium and initial concentration of MB, respectively, in the aqueous phase (mg/L), V is the volume of solution (L), and M is the amount of used solid (g).

2.4. Regeneration process

The used process consists of attractive and effective method based high oxidation potential radical (SO_4^-) for

deconstructing the chemical structures of the removed MB41 on the biomass surface, a solution of Co^{2+} /oxone was employed. The oxone is the source of sulfate radicals, and Co^{2+} acts as a catalyst [14]. This method has not been tested for the biomass regeneration. It consists of treating the FPS sample with a solution of MB (200 mg/L) for 6 h. Then, the sample was separated by filtration, and treated with a mixture of oxone and cobalt solution for 2 h. Once the solid was recovered, the treated solid was immersed to a fresh dye solution for removal in the successive cycle. After that, the sample was filtered, then added to a fresh MB solution with C_i of 200 mg/L for 6 h. The same procedure was repeated for 6–7 runs. The removal percentage was calculated as reported in Eq. (2).

2.5. Characterization

Bruker advance 8 diffractometer (Karlsruhe, Germany), equipped with Ni filter and $\text{Cu K}\alpha$ radiation (0.15418 nm) was used to collect the XRD patterns of the materials. The functional groups present in the materials were analyzed by FTIR, model IR Affinity-1S Shimadzu spectrometer (Tokyo, Japan), in the range of 400–4,000 cm^{-1} , with KBr usage technique. The shape, texture, and the particle size were analyzed by JEM-1400 SEM installed with EDX system (Tokyo, Japan). Thermogravimetric (TG/DTG) analyses were performed using a TA instrument analyzer, model SDT2960 (New Castle, DE, USA), with air flow rate of 50 mL/min, with temperature range of 25°C–800°C at an increasing rate of 10°C/min. Thermo Scientific Genesys 10S UV-vis spectrophotometer (Winsford, UK) at λ_{max} 665 nm was used to investigate the concentration of the solution at equilibrium.

3. Results and discussion

3.1. Characterization of bio-sorbents

The XRD pattern of FPS exhibited one relatively strong broad peak at around 25° and also another weak broad peak at around 43° which is related to the distance at 0.354 and 0.209 nm, respectively (Fig. 1a). The extracted waste (SWP) showed similar pattern as FPS one (Fig. 1b). Upon heat treatment, the XRD patterns indicate that the products are still amorphous with small crystalline domains (Figs. 1c–f). The broad peak at 0.350 nm is attributed to the presence of crystalline cellulose.

The FTIR spectroscopy is an extensively used technique to verify the functional groups that serve as removal sites. FTIR spectrum of the FPS is described in Fig. 2a. Broad band at 3,315 cm^{-1} , related to stretching vibrations of OH groups that bind together by hydrogen bonding, was observed. The cellulose and lignin [15] were believed to be the major contributors to this band, in addition to the water. Temperature treatment affected the intensity of this band. The strong bands in the region of 2,920 and 2,850 cm^{-1} were assigned to the asymmetrical and symmetrical stretching vibrations of CH_2 groups, $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$, respectively, followed by the corresponding $\delta(\text{CH}_2)$ bending vibrations at around 1,468; 1,313; and 725 cm^{-1} . These bands vanished after treatment at 300°C and above (Figs. 2c–f). The intense band at 1,753 cm^{-1} is assigned to C=O stretching mode (esters), upon heat treatment, the band shifted to

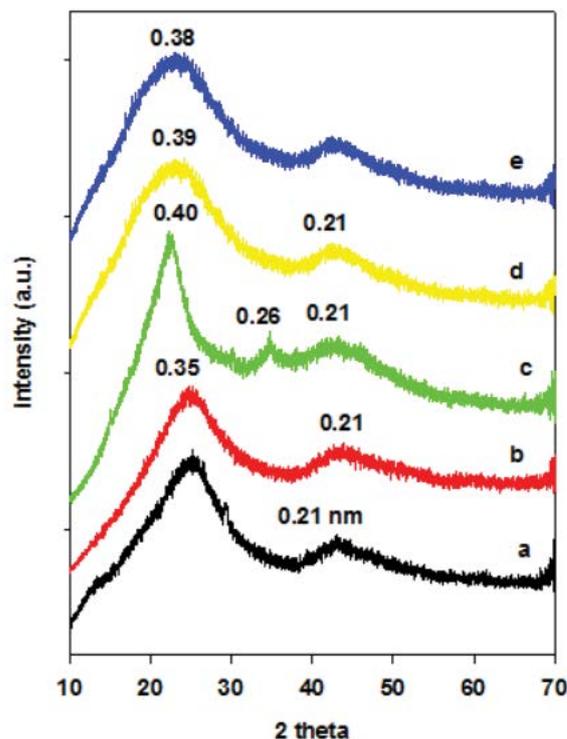


Fig. 1. Powder X-ray diffraction patterns of (a) fresh pine seed (FPS), (b) after extraction (SWP), and treated at different temperatures (c) 200°C, (d) 300°C, (e) 400°C, and (f) 500°C.

higher frequency at 1,710 cm^{-1} , due to the transformation of ester groups to carboxylic groups [16]. The changes to lower wave numbers was ascribed to hydrolysis of esters in natural pine corn during alteration with HNO_3 [20]. After the extraction, SWP material exhibited additional bands at 1,520 and 1,071 cm^{-1} (Fig. 2b). The intensity of these two bands decreased dramatically upon heat treatment, and the sample at 500°C exhibited broad bands 1,580; 1,074; and 800 cm^{-1} , indicating a transformation of SWP waste to different material. It is shown from the FTIR spectra that the transformation of SWP to different materials occurred at temperatures higher than 300°C, further increase in temperature did not lead to further transformation, and similar materials were obtained.

The TGA features of FWP and SWP indicate that these materials behave differently during the heating process. The degradation of SWP occurred in four steps (Fig. 3a) [17]. The moisture evolution occurred from 30°C to 150°C, the hemicelluloses and cellulose decomposition took place in the temperature range of 150°C–370°C, and the lignin decomposition occurred from 370°C to 465°C. The fourth step was assigned to the combustion of the organic matter formed after calcination at 400°C at temperatures higher than 460°C. However, after extraction, the SWP exhibited different behavior, the third step in the range of 370°C–465°C, has disappeared, and it could be related to the loss of some materials during the extraction process (Fig. 3b). Meanwhile, the other two mass steps were present. The heating process led to different materials than the original ones.

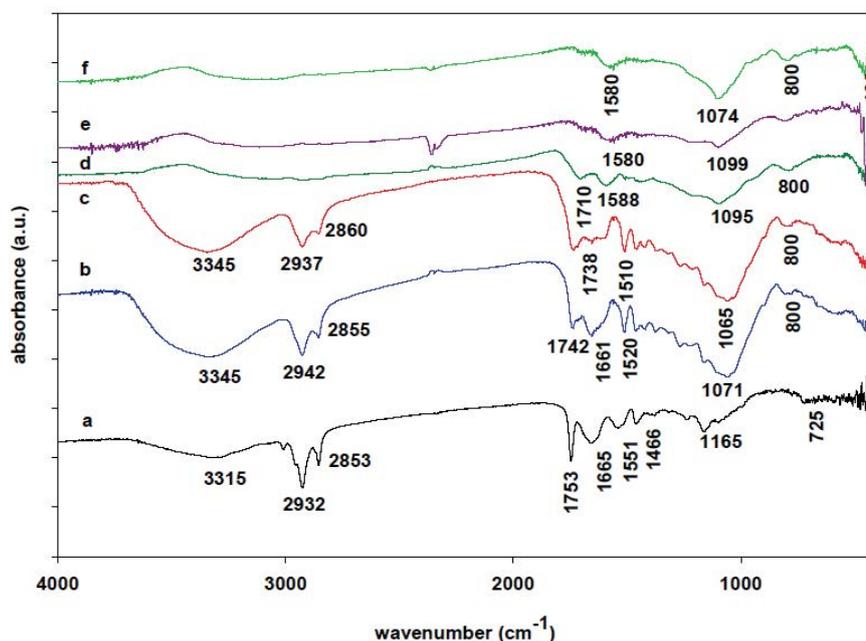


Fig. 2. FTIR spectra of (a) fresh pine seed (FPS), (b) after extraction (SWP), and treated at different temperatures (c) 200°C, (d) 300°C, (e) 400°C, and (f) 500°C.

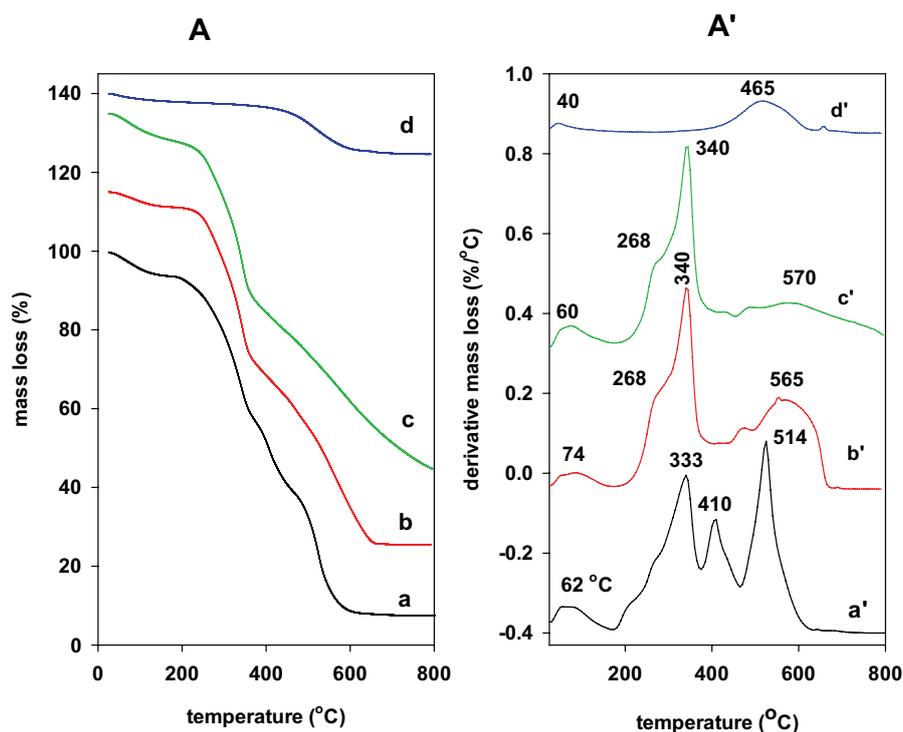


Fig. 3. TGA (A)-DTG (A') features of (a) fresh pine seed (FPS), (b) after extraction (WPS), and treated at different temperatures (c) 200°C, (d) 400°C.

For the samples heated at different temperatures, the TGA features indicated that treatment of the sample at 200°C did not lead significant changes (Fig. 3c). However, after treatment of sample at 300°C, the mass loss in the range of 150°C–370°C disappeared, and continuous mass loss was

recorded at temperatures higher than 370°C. At heating temperature of 400°C, different material exhibited different TGA feature, with only one mass loss step in the range 360°C–650°C, related to a DTG peak at 505°C (Fig. 3d). The sample calcined at 500°C, exhibited low mass loss in all

the temperature range from RT to 800°C, due to the remaining of the non-transformed material (not shown). Even the calcined samples exhibited similar FTIR spectra after treatment at temperatures higher than 300°C, however, under heat treatment they behave differently.

3.2. SEM studies

The SEM examination was carried out to assess the surface structure of the samples. The FPS exhibited spherical shape particles (embryo) embedded in smooth outer coat phase [18] (Fig. 4a). The SWP exhibited different structure, due to the way of grinding that made the particles very small, and only almost the smooth skin coat was detected (Fig. 4b). Fig. 4c indicates that the smooth skin was detected at thermal treatment at 500°C with creation of porous spherical shape, due to the loss of volatile materials leaving the parent sphere structure of the SWP. The EDX analysis indicated that both samples FPS and SWP were mainly formed of carbon (C) varying from 79% to 83%, with 18% to 14% of oxygen (O), and traces of phosphorous (P), magnesium (Mg), and potassium (K) were also detected. Similar results were reported for other biomass wastes with carbon and oxygen as the major constituents [19].

3.3. Removal properties

3.3.1. Effect of initial concentration

The initial concentration is essentially a vital role which supplies the required driving force to conquer the resistance of MB amount transferred between the solid and the aqueous phases [20], since a known mass of adsorbent is able to remove certain quantity of the adsorbate. To evaluate the effects of initial MB concentration on the removal process, SWP (10.0 mg) was added to MB solutions (10.0 mL) of different initial concentrations (from 25 to 1,000 mg/L), at natural pH, and mixed for overnight at room temperature. It has been shown that the removal capacity of SWP improved from 2.03 to 57.32 mg/g, with an increase in MB initial concentration from 10 to 1,000 mg/L. (Fig. 5a). The active sites of the SWP contributed to the relatively high removal, then the efficiency of SWP for MB increased slowly at initial concentrations of MB higher than 700 mg/L. At lower concentrations, the quantity of active sites on the surface against the total dye molecules in the solution is high, therefore all of the dye molecules interact with the SWP. At higher concentrations, not all the MB species will be available to contact with the active surface sites that were already filled up [21]. Simultaneously, the removal percentage of

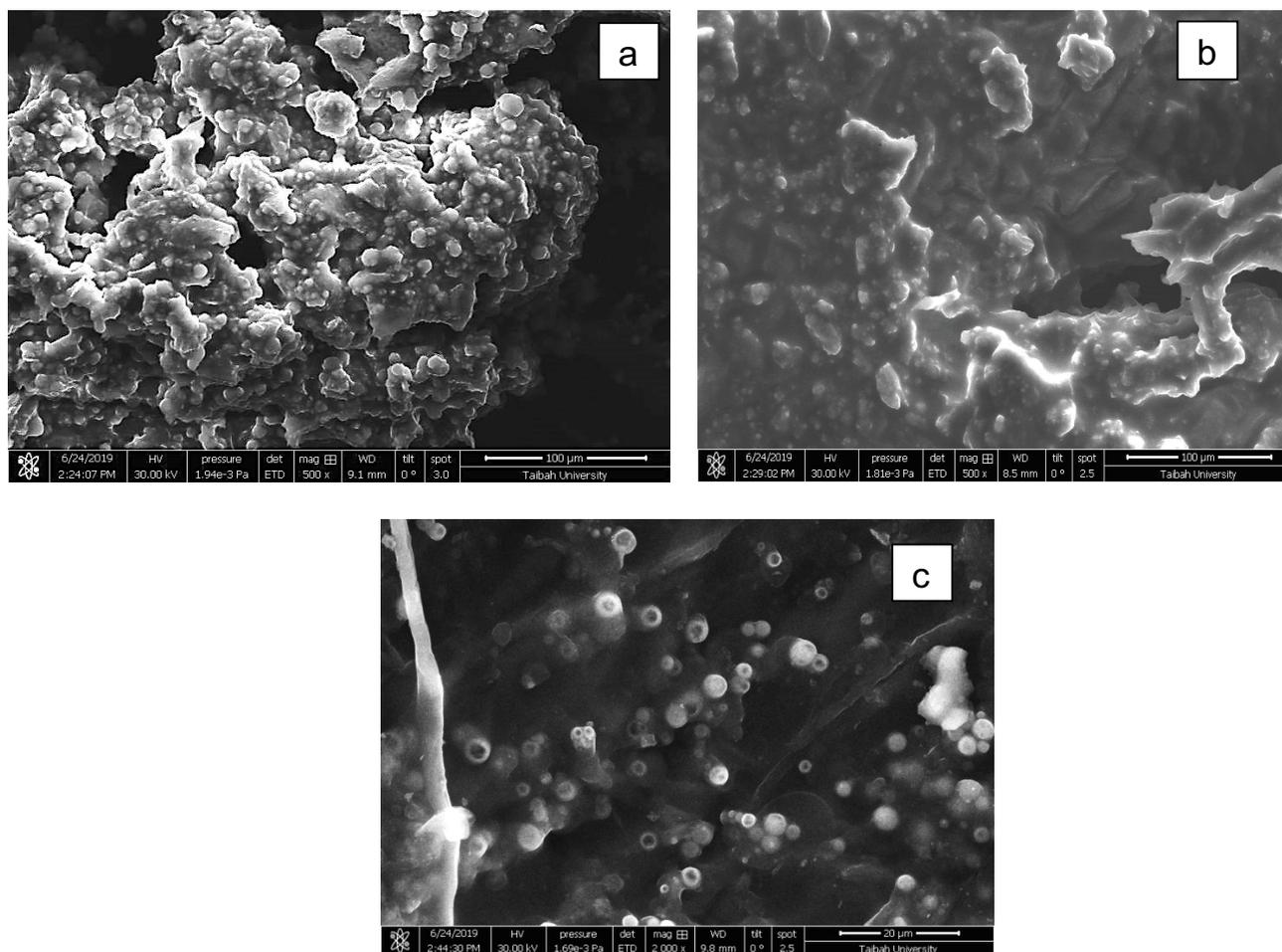


Fig. 4. SEM micrographs of (a) fresh pine seed (FPS), (b) after extraction (SWP), and heat-treated at (c) 500°C.

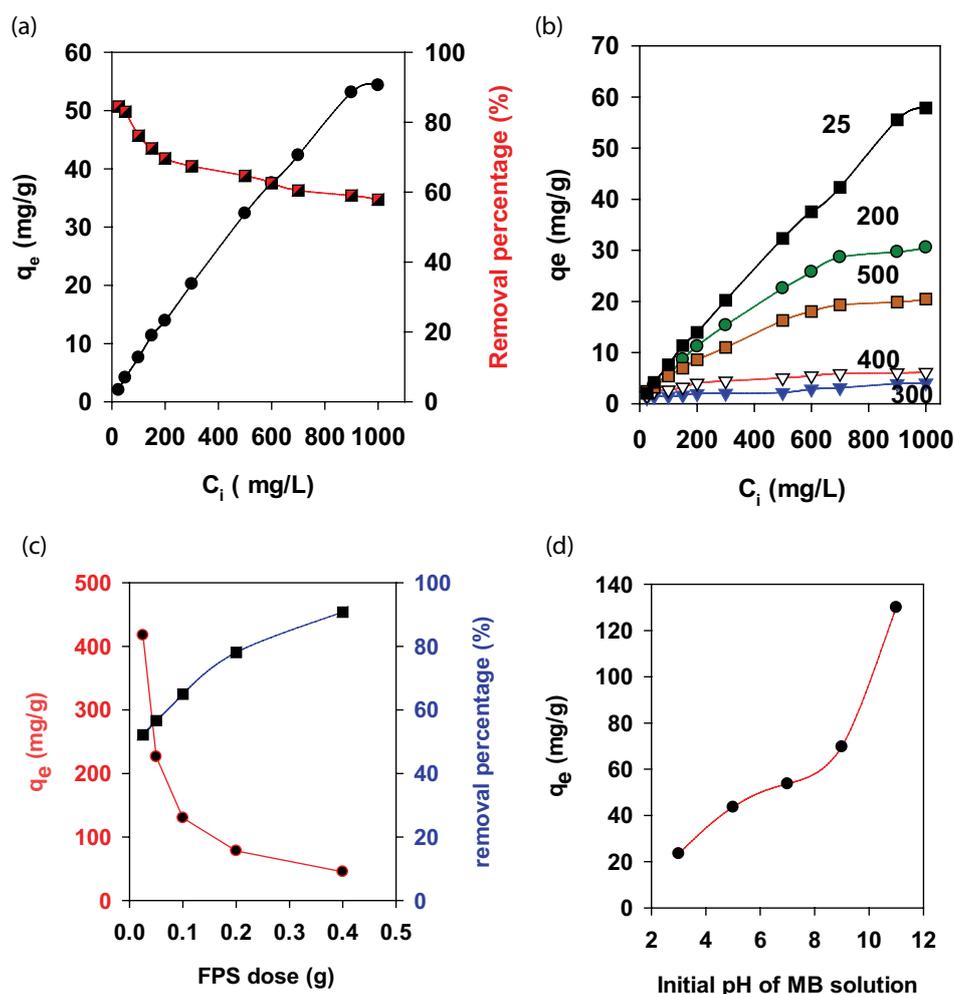


Fig. 5. Effect of (a) MB dye initial concentration on the removal properties of FPS material, (b) heat treatment temperature (°C) of SWP on the removal properties of MB, (c) FPS dose, on the removal of MB, using initial concentration of 200 mg/L, and (d) pH effect of MB solution on its removal percentage using FPS sample.

MB decreased from 90% to 36% with increasing the initial concentrations from 25 to 1,000 mg/L. The decrease was related to the saturation of adsorption sites on the adsorbent surface. Similar data were reported using different solids [13,22,23]. Similar behavior was observed for all the used materials and was in good agreement with other materials.

3.3.2. Effect of pre-calcination

Fig. 5b depicts the changes of MB removal efficiency when the waste pine (SWP) was pre-heated at different temperatures from 200°C to 500°C. After juice extraction, the generated waste (SWP) removed less amount of MB (30.2 mg/g) compared to the pristine one (53.1 mg/g). The efficiency was significantly reduced from a maximum of 30.2–6.1 mg/g when the sample was pre-heated between 200°C and 400°C. Interestingly, an improvement of the removal amount was observed from 7 to 21 mg/g when the sample is heated at 500°C. The variation in the removal properties could be related to the changes on the surfaces of the obtained materials with some loss of the functional groups necessary to the removal of MB dyes. Indeed, it was

reported that the amounts of surface acid oxygen-containing functional groups significantly decreased with increasing pyrolysis temperature from 300°C to 600°C, on different biochars [24]. The cellulose in biomass mainly produces volatiles within the pyrolysis process, while the lignin mainly generates fixed carbon [25].

3.3.3. Effect of SWP dosage

To determine the minimum amount of adsorbent required for removing dye, it is vital to study the consequence of adsorbent dose on MB removal process [26]. Therefore, the effect of FPS doses from 25 to 400 mg in the removal of MB dye was studied. From Fig. 5c, by increasing the dose of FPS at a fixed C_i of 200 mg/L, the removal percentage (%) of MB dye was improved, and it might be ascribed to larger surface area and large number of vacant adsorption sites hence favoring more MB removal [26]. However, the decrease in the removed amount was observed from 417 to 45 mg/g, for MB dye. This fact was extensively reported in literature. The decrease in the amount of the removed dye was the result of the split in the flux of the concentration gradient between the solute

concentration in the surface of SWP and solute concentration in the solution, or to the considerable unsaturation of adsorption sites at high adsorbent dosages [27,28].

3.3.4. Effect of pH

Solution pH has a marked effect on the removal process, especially for dyes, because it can influence the surface charge of the adsorbent, and also the magnitude of the electrostatic charges imparted by the ionized dye molecules. Fig. 5d indicates that the removal amount of MB was improved when the pH of the solution was raised from 4 to 11 with a maximum removed amount of 110 mg/g.

It was reported in literature that MB was a very weak base and reacted only in strong acid solutions to yield low amounts of protonated cations; hence, it was deemed that MB is a positively charged, unprotonated cation, all the way through the pH range examined, with pK_a values of 3.8 and 5.8 [29,30]. The higher removed amounts resulted from the strong electrostatic attractions linking the MB cations and the negatively charged surfaces of SWP. The negative charge of the SWP resulted from the deprotonation of the carboxyl and other functional groups existed on the SWP surface [31]. Since pK_a values of carboxylic acids varied from 3.8 to 5, the amino groups with pK_a of 9.39, and the hydroxyl groups with pK_a value of 8.3, these functional groups would be less protonated.

3.3.5. Effect of removal temperature

Temperature is one of the key parts in the removal method because it affects the solubility of dye molecules in aqueous solution, mobility, and the surface properties of the adsorbent. Additionally, the increase in temperature causes an increased rate of diffusion of the adsorbate molecules across the external boundary layer of the adsorbent particles and inside their internal pores, escorted with reduced solution viscosity [32].

The effect of temperature on the removal of MB dye was studied within the temperatures (20°C, 40°C, 50°C, and 60°C) using C_i of 200 mg/L at a pH 11. The removal of MB improved significantly with the raise of temperature from 20°C to 60°C. The improvement of removal efficiency was ascribed to the activation of the removal sites on the surface of SWP and to the increase of the MB mobility in the solution. Increasing the removal efficiency with increase of temperature indicates an endothermic process in nature. Moreover, by increasing the temperature, the swelling effect may be produced inside the internal structure of SWP enabling dye molecule to go through further.

Table 1
Thermodynamic parameters for the removal of MB by pristine pine seeds

T (K)	K	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol·K)
298	1.857	-1.559		
313	2.903	-2.862		
323	3.956	-3.807	31.57	112.07
333	10.547	-6.522		

Thermodynamic calculations were carried out to find the nature of MB removal technique. The Thermodynamic parameters were worked out using the following Eq. [31].

$$K_c = \frac{C_{ac}}{C_e} \quad (3)$$

$$\Delta G^\circ = -RT \ln K_c \quad (4)$$

$$\log K_c = \left(\frac{\Delta S^\circ}{2.303R} \right) - \left(\frac{\Delta H^\circ}{2.303RT} \right) \quad (5)$$

where C_{ac} and C_e are the equilibrium concentrations (mg/L) of the MB on the SWP surface and in the solution respectively, and K_c is the equilibrium constant. R is gas constant (8.314 J/mol K) and T is the temperature in Kelvin.

The values of ΔH° and ΔS° were calculated from the slope and intercept of van't Hoff plot of $\log K_c$ vs. $1/T$ [31]. The results are presented in Table 1.

The removal of MB was an endothermic process with enthalpy (ΔH°) being 31.57 kJ/mol. An increase in negativity in the Gibbs free energy (ΔG°) with temperature suggests a spontaneous adsorption process. The entropy (ΔS°) of 112.07 J/mol K indicates an increase in the chances of the solid/solution interface during the removal of MB.

3.3.6. Isotherm model and maximum removal

When dealing with adsorption isotherm study, adsorption isotherm equations are typically used including Freundlich, Langmuir, Brunauer–Emmett–Teller, and Redlich–Peterson equation [33]. For the liquid–solid system, the Langmuir and Freundlich isotherm equations are typically engaged. In this study, the Langmuir equation was used to

Table 2
Langmuir parameters estimated from the removal of MB on the different materials

Samples	q_m (mg/g)	K_L (g/mg)	R^2
FPS	85.476	0.0039	0.9996
SWP	35.08	0.0088	0.9994
SWP (200)	7.18	0.0142	0.9987
SWP (300)	4.52	0.0042	0.9981
SWP (400)	6.55	0.0112	0.9956
SWP (500)	24.34	0.0061	0.9991

estimate the maximum removal capacity of the different bio wastes [14], and to optimize the design of a batch reactor.

The assumptions by the Langmuir theory is that sorption takes place at specific sites within the adsorbent, this means that once a dye molecule engages a site, no more adsorption is able to take place at that site. Hence, at equilibrium, a saturation point is accomplished beyond which no further adsorption can take place and the saturation monolayer can therefore be represented by the following equation [34]:

$$K_c \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (6)$$

where K_L is the affinity constant (L/mg), C_e is the solution concentration at equilibrium (mg/L), and q_m is the maximum amount of adsorption (mg/g).

Table 3 summarizes the Langmuir parameters estimated from the removal of MB on the studied materials. The R^2 values were all higher than 0.99, representing a fine mathematical fit, except for materials pre-heated at 300°C and 400°C. The fact that the Langmuir isotherm fits well with the experimental data could be due to homogenous distribution of active sites, and the formation of monolayer of MB cations on the waste surfaces. The maximum removal capacity was obtained for the fresh FPS sample, then it decreased after extraction and heating at temperatures less than 400°C. At higher calcination temperature of 500°C, the removal amount increased, however, still less than the starting material. The decrease in the MB removal amount could be assigned to the loss of some sites necessary to the removal process either by water soaking or by heat treatment. As mentioned above in section 3.3.4., the temperature values affected the acidity of the calcined materials and led to an increase in pH values at higher temperatures, resulting in an improvement of the removal capacities.

Table 3
Comparison of removal capacity of various biosorbents for MB dye

Biosorbent	Removal capacity (mg/g)	Reference
Palm-trees waste	8.4	[35]
Neem leaf	8.7–19.6	[36]
Pomegranate peels	200	[19]
Date stones	8.8	[35]
Watermelon rinds	188	[31]
dragon fruit peels	139	[37]
Yellow passion fruit	14.0	[38]
Wheat shells	16.5–21.5	[39]
Mansonia wood sawdust	8.5–28.0	[40]
Rice husk	40.5	[41]
Corn husk	18.0–41.5	[28]
Coconut bunch	30.4–65.5	[42]
Coconut leaf	112.3	[13]
Pristine pine seeds	85.6	This study
Extract pine seeds	35.2	This work

The potential of pine wastes was evaluated by comparing the removal capacity of MB onto various biomass wastes (Table 4). The pristine pine seeds exhibited reasonable removal capacity of 85 mg/g, and this value is higher or comparable with the data reported in Table 4. This could indicate that SWP can be regarded as effective material for the removal of MB dye. The difference between the reported data, could be related to the removal conditions, or to distribution of removal sites on mentioned materials. The extraction of the juice from the SWP negatively affected the MB uptake, and a decrease of q_{max} was observed.

The adsorption of MB was examined by FTIR technique (figure not shown). The overall feature of the spectra before and after removal of MB was unchanged, indicating that the removal of MB did not change the surface chemical properties of the biosorbent [43]. In an aqueous solution, MB cations can accumulate in the form of monomers, dimers, trimers, and tetramers depending on the concentration of MB in water [44]. The absorption spectra of the net MB solutions at the used concentrations range exhibited two absorption maxima at 660 and 610 nm corresponding to the monomer and dimer of MB, respectively [45], suggesting that MB molecules exist in solution mainly in the form of monomer (MB^+) and dimer (MB_2^{2+}) cations. In the literature, the removal of MB occurred either by electrostatic interaction between the MB cations and the negatively charged adsorption sites, or to hydrogen bonding between the dye molecules and the adsorption sites [46,47]. In our case, the variation of pH values of the solution has affected the removal amount, and it could be related to the change of the type of the surface charges and thus the electrostatic interaction between MB and pine waste surfaces.

4. Regeneration studies

Different regeneration schemes of bio-sorbents were reported in the literature and summarized in a recent review [48]. The regeneration scheme is vital for maintaining the charge of the procedure down and opening the possibility of retrieve the contaminant separated from the stream. As mentioned in section 2.4 (regeneration process), sulfate radical oxidation was proposed, in which Co^{2+} /oxone was employed to regenerate the used materials. The fresh waste pine (FPS) and the resulting (SWP) materials were used in this part. The fresh wastes were in contact with MB solution ($C_i = 200$ mg/L), separated by centrifugation, and treated in oxone and cobalt nitrate solutions. This method induced the degradation of the absorbed MB and per consequent, restoring the initial removal capacity of the adsorbent materials. Then, the sample was added again to MB solution with C_i of 200 mg/L, for another removal cycle. This regeneration–reuse process was repeated 5–7 times.

Fig. 6 indicates that the removal percentage of FPS (45%) was slightly changed after four cycles, with an efficiency of 38%, at the fourth cycle. However, for the SWP spent material (Fig. 6), the starting percentage of MB removal (22%) was maintained only for three cycles with a decrease to 15%. Further regeneration cycles, led to a significant reduction of the removal percentage for both materials. However, the FPS exhibited higher values than the SWP spent material. Increasing the number of regeneration runs affects the

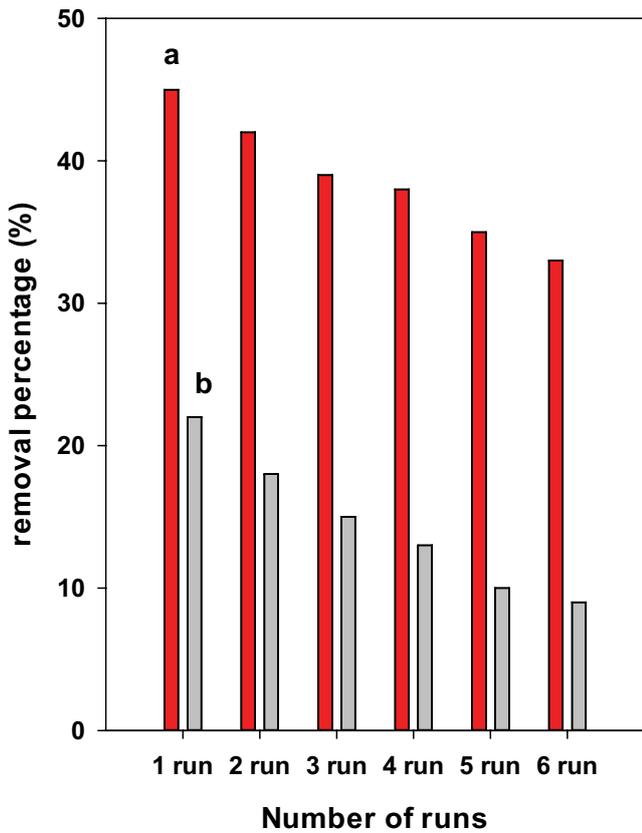


Fig. 6. Regeneration properties of (a) FPS and (b) SWP samples using an MB initial concentration of 200 mg/L.

adsorption ability of waste materials. This fact could be related to the solid degradation and deactivation of some reactive sites after each regeneration run [49], or to strongly adsorbed MB species which were incompletely destroyed during the treatment of oxone and cobalt solution, leading to a decrease of free removal sites.

5. Design of single-stage batch removal from isotherm data

The empirical design procedure was proposed as a general method to predict the adsorbent size and performance of the used material. The lack of extensive experimental data and adsorption isotherm studies could not foresee these properties effectively. The design objective was to minimize the solid adsorbent for a specific volume of initial concentration [50].

Consider an effluent containing V (L) of solution and let the dye concentration get reduced from C_0 to C_1 mg dye/L solution. For an amount of adsorbent m (g), the solute loading changed from q_0 to q_1 (mg dye/g adsorbent). When fresh adsorbent is used, $q_0 = 0$, the mass balance for the MB dye in the single-stage operation under equilibrium is given by Eq. (7):

$$V(C_0 - C_e) = m(q_0 - q_e) = mq_e \tag{7}$$

In the present case the removal of Methylene blue fitted well with the Langmuir isotherm. Consequently, the Langmuir equation can be substituted in Eq. (7), and the rearranged form is presented in Eq. (8) [51].

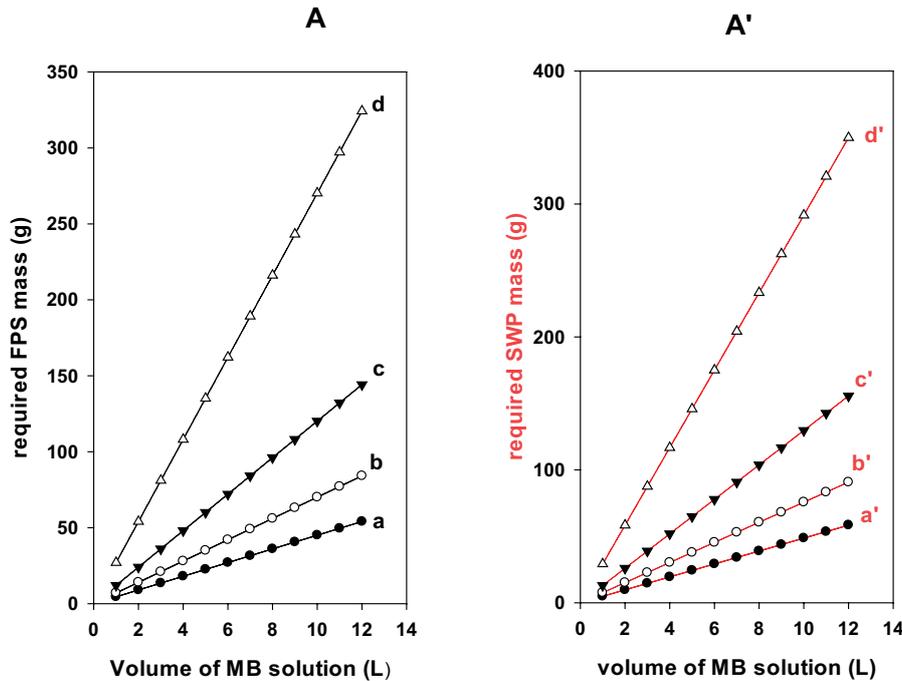


Fig. 7. Design plot (A) for FPS and (A') for SWP, generated using Langmuir isotherm model for different MB solution volumes at different removal percentages (a and a') 60%, (b and b') 70%, (c and c') 80%, and (d and d') 90%, for a fixed initial concentration of 200 mg/L.

$$\frac{m}{V} = \frac{C_0 - C_e}{q_e} = \frac{C_0 - C_e}{\frac{q_m K_L C_e}{1 + K_L C_e}} \quad (8)$$

Eq. (8) could be used in the design objective to treat a fixed volume of 12 L of 200 mg/L MB solution, for a removal dye removal assumption of 90%. It is required 324 and 350 g of SWP and WSP, respectively. Fig. 7 depicts the plots derived from Eq. (8) to predict the required (g) amount of waste pine to treat different effluent volumes from 1 to 12 L in 1 L increment, at an initial MB dye concentrations of 200 mg/L, for different percentages removal (60%–90%). The amount of waste pines can be estimated within the range of 54–350 g and solution volume range of 1–12 L. These data indicated also that the two wastes exhibited similar removal properties, when they were used at higher amounts, and it could promote the utility of both FPS and SWP as removal agents for MB.

6. Conclusions

The fresh FPS before and after extraction of its juice (SWP) were proposed as removal agents of methylene blue, the effect of different conditions was investigated, The pre-heat treatment in the range of 200°C–400°C, led to a reduction of the removal efficiency from 30 to 7 mg/g, with an improvement after a pre-heat treatment at 500°C. The optimal conditions to achieve maximum amount of removal for MB were identified, a highest value of 110 mg/g was accomplished at pH 11 and at room temperature.

The regeneration tests indicated that the used material (SWP) was stable after five cycles of regeneration, meanwhile, the removal efficiency was lost for SWP after three recycles of removal. The removal agent and handling costs will be reduced using the batch adsorber design, based on the Langmuir model and the maximum removal capacity. The two used wastes behave in close manner, and they could be proposed as alternative low-cost removal agents.

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