



## ORIGINAL ARTICLE

# Facile synthesis of eco-friendly activated carbon from leaves of sugar beet waste as a superior nonconventional adsorbent for anionic and cationic dyes from aqueous solutions



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**Abstract** The current study presents a unique and innovative approach to sustainable activated carbon (AC) synthesis using non-conventional agricultural wastes, leaves of sugar beet (LSB), via a thermo-chemical activation process. This approach not only offers a sustainable solution for LSB elimination, but also provides an eco-friendly alternative to commercially available activated carbon. The thermo-chemical activation process was conducted at various ratios of H<sub>3</sub>PO<sub>4</sub> / LSB (0.5:1, 1:1, 2:1, and 3:1 w/w ratios) at a fixed temperature (550 °C/2h). The unique amorphous nature, porous structure, BET surface area (S<sub>BET</sub> = 700.7 m<sup>2</sup>/g), and surface chemistry nominated the synthesized AC at 2:1 ratio as a superior adsorbent material for methyl orange, MO, and methylene blue, MB, from standard solutions in the batch system at different experimental conditions. Kinetic investigations revealed that the pseudo-second order equation explained the sorption data well. In contrast, intra-particle diffusion was not the only limiting stage in the adsorption of the addressed dyes. Similarly, the linear Langmuir equation described the adsorption data of the investigated dyes better than Freundlich one with maximum removal capacity (q<sub>max</sub>) of 185.2 and 140.8 mg/g for MB and MO, orderly. This confirms the homogenous/monolayer nature of the adsorbed ions through isoenergetic active sites upon the AC<sub>(2:1)</sub> surface. Furthermore, the electrostatic attraction was not the only leading mechanism of adsorption of both dyes, but substantial

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participations by hydrophobic hydrogen-bonding forces may be considered.

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## 1. Introduction

AC (Activated carbon) is a type of carbonaceous material with unique characteristics such as high physicochemical stability, high porosity, mechanical strength, and a large surface area. There are numerous applications for activated carbon (Lewoyehu, 2021), including pharmaceutical (Subha and Namasivayam, 2009; Zhu et al., 2022), nuclear power stations (Kato et al., 2022), catalysis (Azargohar and Dalai, 2006; Marandi et al., 2022), separation, purification (Manoochehri et al., 2012; Natrayan et al., 2022), chemical and petroleum sectors (Ngofa et al., 2022), water treatment (Yuan et al., 2022) and others. AC is produced by oxidizing atoms found on elemental carbon's outer and inner surfaces (Al-Qodah and Shawabkah, 2009; Chatir et al., 2022; Dias et al., 2007; Guo et al., 2009; Ho et al., 2009; Idris et al., 2012; Jin et al., 2010; Sahu et al., 2010; Yahya et al., 2015). Two main distinct approaches are familiar for activated carbon production: physical and chemical preparation (Danish et al., 2011; Ekpete and Horsfall, 2011; Gayathiri et al., 2022; Hoang et al., 2022). The physical approach "dry activation," comprises two successive stages: carbonization (below 700 °C) and activation (up to 1100 °C) (Heidarinejad et al., 2020; Ketcha et al., 2012). Carbonization decreases the volatile elements of the precursor material to produce char with a more extensive fixed content of carbon. Also, the atoms of carbon undergo graphitic-like reordering during the carbonization process. The resulting charcoal is not an active product but has initial porosity and low surface area (Nazem et al., 2020). In the activation step, the carbonized charcoal reacts with oxidizing gases such as H<sub>2</sub>O (steam), air, CO<sub>2</sub> (carbon dioxide), or any mixture of these gases, therefore carbon oxides are evolved from the carbon surfaces (León et al., 2020). This is a heterogeneous and complicated process that involves the transportation of gases to the surface of the charcoal, circulation into their pores, sorption upon the pore surface, reaction with carbon, desorption, and diffusion of the prepared products into the air (Baseri et al., 2012; Sekirifa et al., 2013). But, it requires a higher activation temperature, longer activation time, and low porosity (Husien et al., 2022; Kilpimaa et al., 2015). In chemical activation "wet oxidation", the impregnation of the precursor into the selected activation agent then washing to create activated carbon, is conducted. This process needs approximately low temperatures (450 to 600 °C) and mainly relies on the capability of inorganic additives to dehydrate and degrade the cellulosic elements of the precursor (Kalderis et al., 2008; Merzougui and Addoun, 2008; Wang et al., 2022). H<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>S, KCNS (Demiral et al., 2008; Goswami and Dey, 2022), NaOH, KOH (Kielbasa et al., 2022; Zhengrong and Xiaomin, 2013) HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, KMnO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (Al-Qodah and Shawabkah, 2009; Guo et al., 2023; Luo et al.), K<sub>2</sub>CO<sub>3</sub> (Adinata et al., 2007; Jasri et al., 2023), ZnCl<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> (Cruz et al., 2012; Joseph et al., 2006; Karapinar, 2022) are the most commonly employed oxidizing agents (chemical catalysts). When the precursor reacts with activating agents, the oxygen groups can be added to the carbon of the precursor (Yahya et al., 2015). Depending on the employed chemical reagents, washing with acid or alkali is essentially the final step in the activation process (Md Zaini et al., 2023). This is succeeded by distilled water washing to discard the trapped chemicals in the AC porous structure (Albatrni et al., 2022). Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) has become the most popular activating agent in recent years for environmental and economic reasons (Chatir et al., 2022; El Qada et al., 2008; Ferreira et al., 2022; Neme et al., 2022). It contributes to the production of AC with enhanced mesopores and micropores (Danish et al., 2014a; Ozpinar et al.,

2022). H<sub>3</sub>PO<sub>4</sub> was predominantly utilized on lignocellulosic woody materials (Ahmad and Hameed, 2010; Budinova et al., 2006; Sirajo and Ahmad Zaini, 2023), fruits and stones (Danish et al., 2014b; Danish et al., 2022; Gratiuto et al., 2008; Örkün et al., 2012; Prahaz et al., 2008), and agricultural wastes (Corcho-Corral et al., 2006; Guo and Rockstraw, 2007; Ioannidou and Zabaniotou, 2007; Koyuncu et al., 2022; Li et al., 2010; Liou, 2010; Soleimani and Kaghazchi, 2007). Agricultural wastes and carbonaceous natural raw materials offer renewable, biodegradable source for activated carbon production (Karić et al., 2022). The removal efficiency of AC vary depending on the precursor materials and the activation protocol, including pyrolysis time & temperature, content of heteroatom, pore texture, surface area and charge (Tiwari et al., 2022).

Anionic methyl orange (MO) is a heavily applied water-soluble azo-dye in various industrial sectors, such as cosmetics, paper, food processing, leather, and textile (Wang et al., 2019a). The potential of MO dye to possess carcinogenic, teratogenic, and mutagenic properties is suggested (Haque et al., 2021; Sriram et al., 2022), which implies that it has the capability of causing cancer, birth defects, or genetic mutations. In addition, MO is known to be highly recalcitrant in nature, meaning it has low biodegradability and can endure in the environment for extended periods (Arumugam et al., 2022; El-Sheikh et al., 2022a; Mubarak et al., 2022). On the other hand, MB is a synthetic dye used in textile, and medical laboratory applications (Khan et al., 2022; Tuli et al., 2020), but high levels of exposure can be hazardous to human health and the environment. It can cause various adverse effects such as irreversible eye injury, vomiting, gastritis, breathing problems, nausea, cognitive confusion, painful urination, tissue death, bluish discoloration of skin, and a condition resembling methemoglobinemia. Additionally, it is considered highly carcinogenic for living beings (Bayomie et al., 2020; Liu et al., 2021; Nazir et al., 2020; Swaminathan et al., 2015; Ullah et al., 2022). Adsorption can be considered the most efficient and widely applied approach for dye remediation from aquatic environments (Aluigi et al., 2011; Ayad and El-Nasr, 2010; Gupta and Suhas, 2009; Kumar Biswal et al., 2022; Rafatullah et al., 2010; Senthil Kumar et al., 2014; Tan et al., 2008; Yao et al., 2013). This was correlated not only to its low cost but also the simplicity and easiness of operation (Kumar Biswal et al., 2022; Rafatullah et al., 2010).

Sugar beet is a strategic plant for sugar production in Egypt. The annual cultivated areas in Egypt exceed 600,000 acres. Leaves of sugar beet (LSB) represent approximately 40–50% of the harvested materials. They are made mainly of pectin (14–18%), cellulose (13–18%), and hemicellulose (11–17%), with subordinate lignin content (5–6%) and the moisture content of the dried LSB doesn't exceed 5.5%. This composition reflects their enrichment in carbohydrates, proteins, fibers, and mineral elements, such as K, Ca, Na, and Fe (Ninfali and Angelino, 2013). These greens are usually abandoned during beet root harvesting as waste causing a severe environmental problem.

The application of ACs that were produced for the first time from LSB waste, in the remediation of cationic and anionic dyes, was not investigated before. Consequently, the present study was dedicated to: 1) Recycling the widely available LSB waste in the synthesis of sustainable ACs via thermo-chemical activation procedure, and 2) Studying the effect of initial pH, contact time, adsorbent dose, and initial concentration, as the most commonly applied experimental factors, upon the remediation efficiency of cationic (methylene blue) and anionic (methyl orange) dyes by the selected AC form the prepared ones.

## 2. Materials and methods

### 2.1. Materials

The leaves of sugar beet (LSB), a common agro-residue, were collected from some sugar beet farms during harvesting season from February to June at Kom Abo Radi area, Beni-Suef Governorate, Egypt. These wastes are required to synthesize active carbon (AC). Also, 85%  $H_3PO_4$  was delivered from E. Merck, Germany to be applied as an activating agent for LSB during their transformation into ACs via a thermochemical activation process.

### 2.2. LSB preparation

The LSB was soaked overnight in distilled water (DW) to eliminate any adhering dust and other contaminations. After several cycles of washing, the LSB were boiled for coloration removal till getting colorless water. This was succeeded by oven drying for 24 h at 70 °C. The dried LSB sample was intensively ground by mortar and pestle below 100  $\mu m$  and packed tightly for succeeding steps.

### 2.3. Active carbons (ACs) synthesis from agro-residue LSB

To activate the prepared LSB powder using an acid agent, 5 g of this powder was separately and homogeneously blended with different masses of  $H_3PO_4$  (2.5, 5, 10, and 15 g), to satisfy  $H_3PO_4$ / LSB W/W impregnation ratios of 0.5:1, 1:1, 2:1 and 3:1, orderly. Each prepared mix was dissolved in 100 ml of DW and kept at ambient temperature overnight without any disturbance. Each permeated mixture was transferred into a programmable muffle furnace/10 °C per min for 2 h at 550 °C to complete the activation process. With distilled water and NaOH (0.1 M), the produced ACs were washed several times

thoroughly till neutralization. After, drying for 24 h at 70 °C, the AC samples were ground to < 100  $\mu m$  and labeled as AC<sub>(0.5:1)</sub>, (1:1), (2:1)& (3:1) concerning the utilized acid ratio. The sketch compiling the synthesis protocol is depicted in Fig. 1.

### 2.4. Characterization of the precursor LSB and the derivative activated carbons (ACs)

The powder of the precursor LSB and the as-synthesized ACs (< 100  $\mu m$ ) were examined by XRD (APD-3720 diffractometer /Philips/Cu K $\alpha$  radiation/2 $\theta$  range of 5-80°/ scanning speed, 5° each min/ 40 kV and 20 mA), SEM (JSM-6700F/ JEOL/ Japan/energy of used beam from 20 to 30 kV/ working distance from 11.1 to 12.2 mm), FT-IR (Bruker Spectrometer/FTIR-2000/ from 400 to 4000  $cm^{-1}$ / reflection resolution mode 4  $cm^{-1}$ ) techniques to determine their crystalline phases, morphological features, and the distinctive active sites, respectively. Surface Area Analyzer (Quantachrome/ Nova 2000) was used to determine the surface area ( $S_{BET}$ ), average pore diameter ( $D_p$ ), and total pore volume ( $V_t$ ) of the materials of interest following a 2-hour vacuum degassing at 100°Celsius. Brunauer-Emmett-Teller equation was used to calculate the  $S_{BET}$  (Brunauer et al., 1938), whereas the  $D_p$  and  $V_t$  were estimated by Barrett-Joyner-Halenda (BJH) one (Barrett et al., 1951).

### 2.5. Batch system experiments using aqueous solutions

Cationic (methylene blue, MB) and anionic (methyl orange, MO) dyes were selected to be remediated by the selected type of the prepared ACs in the batch system.

One gram of MO and MB was independently dissolved in one liter of distilled water, DW, to get stock solutions of 1.0 g/L. Dilutions of MO and MB stock solutions with DW were made to the appropriate concentrations for the kinetic and equilibrium experiments.

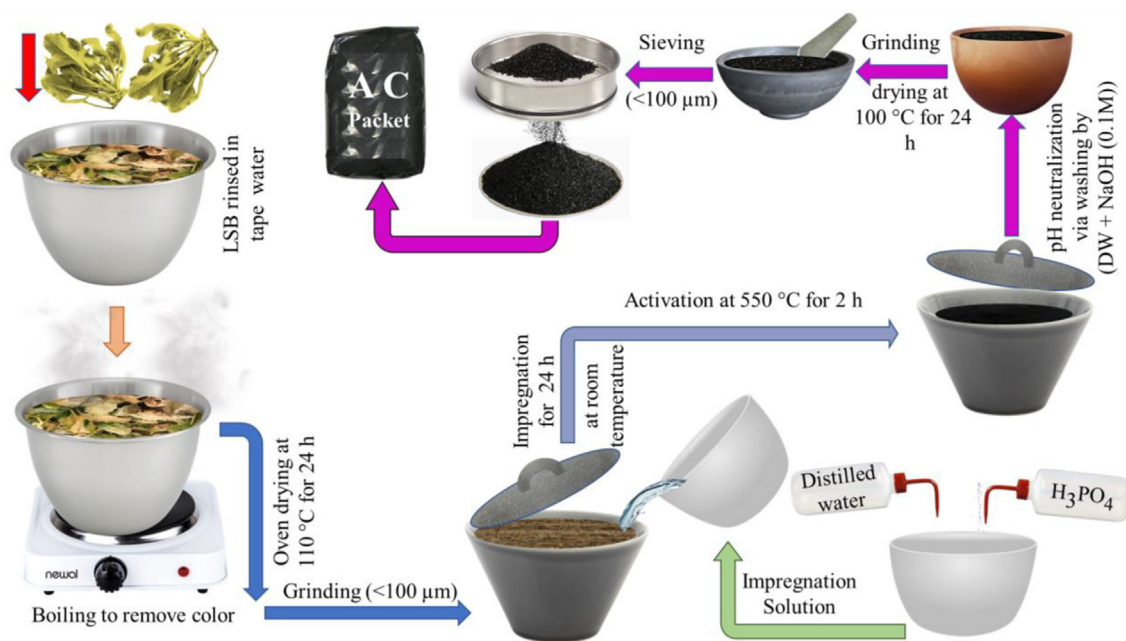


Fig. 1 Sketch summarizing the stages of the ACs production process.

### 2.5.1. Effect of pH

To gauge the ACs (0.5:1- 3:1) removal efficiency in comparison with the precursor LSB (leaves of sugar beet) in removing the selected dyes (MO and MB) from aqueous solutions, several equilibrium experiments were conducted at various pH (2.0–10.0), maintaining the other factors constant as illustrated in Table 1. After centrifuging at 10000 rpm for about 15 min to separate solid from liquid (Mikro 120/Hettich/UK), the concentration of the remaining dyes in the separated liquid phases was measured by DR 6000 spectrophotometer at = 468 nm & 665 nm, for MO and MB, respectively (Mohamed et al., 2019; Subbaiah and Kim, 2016). Equations (1&2) tabulated in Table 2 were utilized to estimate the adsorbed MO and MB amounts ( $q_e$ , mg/g) and the uptake efficiency of the applied AC (%) at equilibrium.

The results of pH experiments, to a great extent helped in deciding which type of the prepared ACs will be used for subsequent investigations.

### 2.5.2. Effect adsorbent dose

To merit the efficiency of the selected AC<sub>(2:1)</sub> in remediating the addressed dyes (MO & MB), the effect of utilized dose (10 to 35 mg), maintaining the other factors fixed as illustrated in Table 1. Similarly, equations 1 and 2 (Table 2), were employed to estimate  $q_e$  (mg/ g), and the uptake efficiency (%) of the applied AC at equilibrium, respectively.

### 2.5.3. Isotherm and kinetic studies

A constant mass (20 mg) of the chosen AC<sub>(2:1)</sub> was independently introduced to 25 ml of MB and MO solutions with various initial concentrations (60 to 160 mg/L) under dynamic shaking (200 rpm)/ 2 h (Table 1) to configure which of the applied isotherm models will explain the data-well. The  $q_e$  (mg/g) of both MO and MB was estimated by equation 1. (Table 2).

The kinetic studies involved a separate addition of 25 mg of the chosen AC<sub>(1:1)</sub> to 25 ml of MO and MB with a fixed initial concentration (120 and 80 mg/L, respectively) and shaking the mixture at 200 rpm for 5, 15, 30, 60, 120, and 240 min (Table 1). Equations 2 and 3 cited in Table 2, were employed to determine the  $q_t$ , (mg/g), and R% of the applied adsorbent for the investigated dyes, orderly.

The experiments were performed at  $25 \pm 3$  °C in triplicate, and the results have been averaged.

## 3. Results and discussion

### 3.1. Characterization of agricultural waste (LSB) and active carbons (ACs)

The XRD patterns of ACs compared to the precursor LSB were depicted in Fig. 2. It was revealed that the broad diffraction background in the derivative ACs which reflects the gained amorphicity after the precursor LSB, was preserved

**Table 1** The applied experimental parameters and the prevailing conditions during the conduction of the MO & MB adsorption experiments by the addressed adsorbents.

Investigated parameter	Conditions						The other parameters
	2	3	5	7	9	10	
pH	2	3	5	7	9	10	100 & 80 mg/L initial conc., for MO& MB, respectively, 25 mg dose, 200 rpm/ 2 h (agitation time /speed), 25 ml solution.
Adsorbent dose (mg)	10	15	20	25	30	35	pH (3.0 & 9.0), 120 & 100 mg/L of MO & MB initial conc., respectively, 200 rpm, 2 h (agitation time /speed), 25 ml solution.
Agitation time (min)	5	15	30	60	120	240	pH (3.0 & 9.0), 120 & 80 mg/L of MO & MB initial conc., respectively, 25 mg dose, 200 rpm/2h (agitation time /speed), 25 ml solution.
MO & MB initial conc., (mg/L)	60	80	100	120	140	160	pH (3.0 & 9.0) for MO & MB, respectively, 20 mg dose, 200 rpm/2h (agitation time / speed), 25 ml solution.

**Table 2** Equilibrium equations that express the MO & MB adsorption by addressed adsorbents.

Equation №	Linear form	Parameters
Eq.1	$q_e = \frac{V(C_i - C_f)}{m}$	$q_e$ (mg/g): sorbed amount of MO & MB at equilibrium $C_i$ : the initial MO & MB concentration in solutions (mg/L) $C_f$ : the concentration of MO & MB at equilibrium (mg/L) $V$ : the volume of MO & MB solutions (mL) $m$ : the mass of adsorbents (mg).
Eq.2	$q_t = \frac{V(C_i - C_t)}{m}$	$q_t$ (mg/g): sorbed amount of MO & MB at time t $C_i$ : the initial MO & MB concentration in solutions (mg/L) $C_t$ : the concentration of MO (mg/L) at time t $V$ : the volume of MO & MB solutions (mL) $m$ : the mass of adsorbents (mg)
Eq.3	$R\% = \frac{(C_i - C_t)}{C_i} \times 100$	$R\%$ : removal efficiency of MO & MB by addressed adsorbent $C_i$ : the initial MO& MB concentration in solutions (mg/L) $C_t$ : the concentration of MO & MB (mg/L) at time t

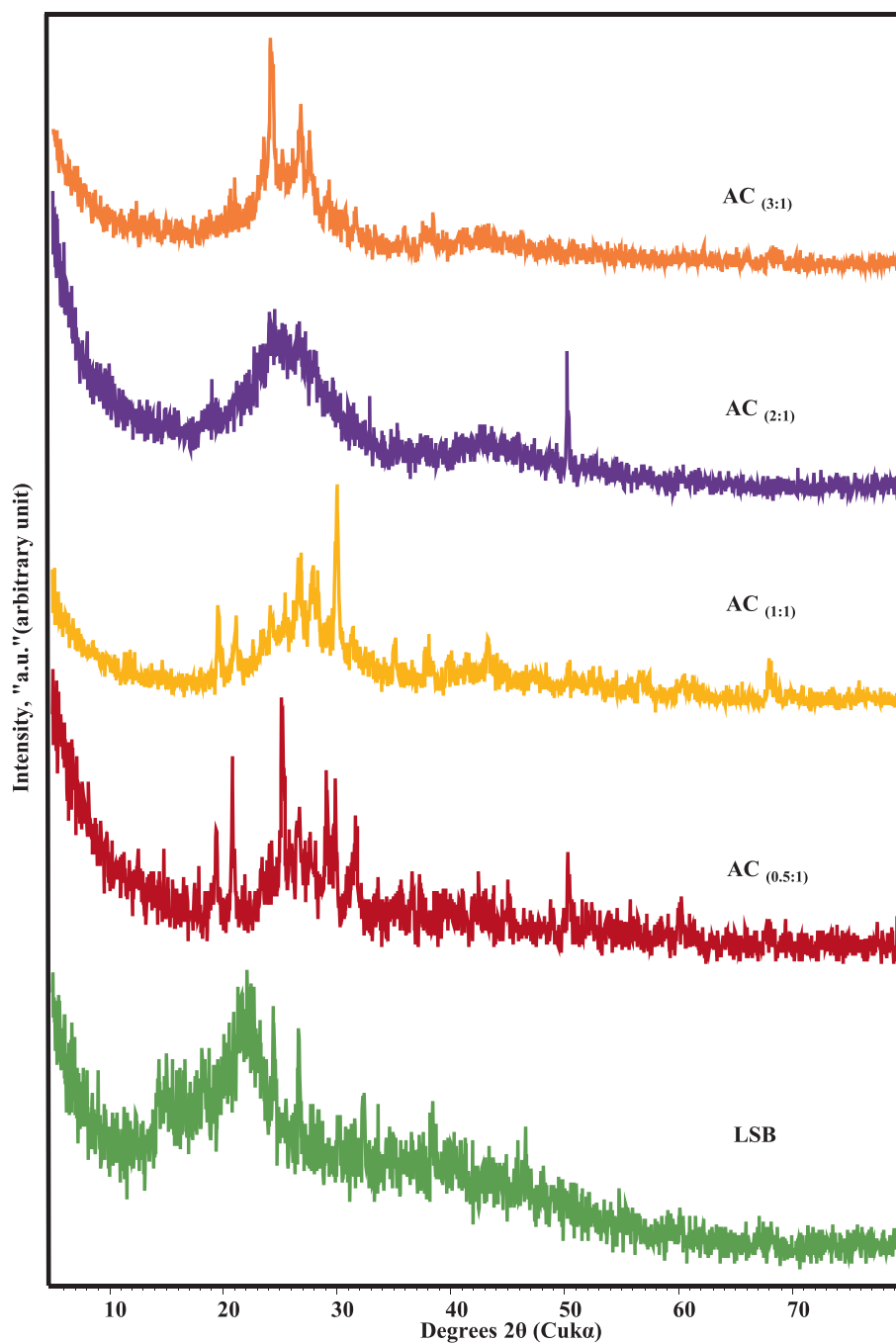


Fig. 2 XRD patterns of the synthesized ACs in comparison with the precursor LSB.

but with less magnitude and slight shifting in  $2\theta$  values (from 20 to  $30^\circ$  instead of  $20\text{--}25^\circ$  in LSB) (Shamsuddin et al., 2016). However, some signs of improved crystallinity were traced in the derivative ACs through the emergence of some minor peaks at  $2\theta \approx 19.37\text{--}19.58$  &  $20.79\text{--}21.10^\circ$ . These latter peaks could be ascribed to the  $\gamma$ -phase carbon (Burgess-Clifford et al., 2009; Mohamed et al., 2020). Nevertheless, the peak intensity of this crystalline phase was reduced with the gradual rise of the utilized acid concentration till the entire absence in  $AC_{(2:1)}$ . Furthermore, the biogenic crystalline silica in the LSB that was reflected by the moderate peak at  $2\theta = 26.7^\circ$  (Zayed et al., 2020), was masked by the approximately vital

reflection plane (002) of graphite in the derivative  $AC_{(0.5:1)}$ ,  $AC_{(1:1)}$  &  $AC_{(3:1)}$ , at  $2\theta \approx 26.57$ ,  $26.56$  &  $26.69^\circ$ , with  $d_{(002)} \approx 3.34\text{--}3.36$  Å, respectively. Such reflection plane (002) is approximately missing in  $AC_{(1:2)}$  pattern as a sign of low graphitization degree. Meanwhile, the weak peaks around  $2\theta \approx 42\text{--}43^\circ$  in  $AC_{(1:1)}$ ,  $AC_{(2:1)}$  &  $AC_{(3:1)}$ , might be unrelated to the graphite reflection plane (101);  $d_{(101)} \approx 2.09\text{--}2.14$  Å. Therefore, the peaks around  $26^\circ$  and  $43^\circ$  in the prepared ACs, symbolize their amorphous nature, especially in  $AC_{(2:1)}$  (Xu et al., 2014). This indicates the crucial role of the utilized  $H_3PO_4$  acid upon the graphitization degree of the ACs through the production of a more orderly arranged and densely packed microcrystalline

structure (Zhang et al., 2018). So, the applied acid not only acted as a dehydrating agent which affected the pyrolytic breakdown of LSB, but also impeded the ash development and improved carbon yield (Omri and Benzina, 2012). However, this attitude is not applicable for AC<sub>(2:1)</sub> but the amorphous nature prevails. On the level of the non-carbonaceous phase, the occurrence of a small quantity of the remaining ash after the activation process, especially at low acid concentrations, AC<sub>(0.5:1)</sub> & (1:1), was reflected by the emergence of

minor peaks of quartz at  $2\theta \approx 50.35\text{--}51.25$ ,  $60.19\text{--}60.33$  and  $68.01^\circ$ . Conversely, at the highest acid ratio (AC<sub>(3:1)</sub>), the amount of the ash remains was exceptionally minimized (Fig. 2). However, at AC<sub>(1:2)</sub>, the presence of such silicious ash was expressed at  $2\theta \approx 50.2^\circ$  as a powerful peak. The other non-carbonaceous phase is calcite that was recorded in the patterns of ACs that was formed at low acid ratios (AC<sub>(0.5:1)</sub> & (1:1)). This phase was emerged at  $2\theta \approx 29.4\text{--}29.9$  and  $30.02^\circ$ , respectively, in response of enlarged calcium occurrence of the

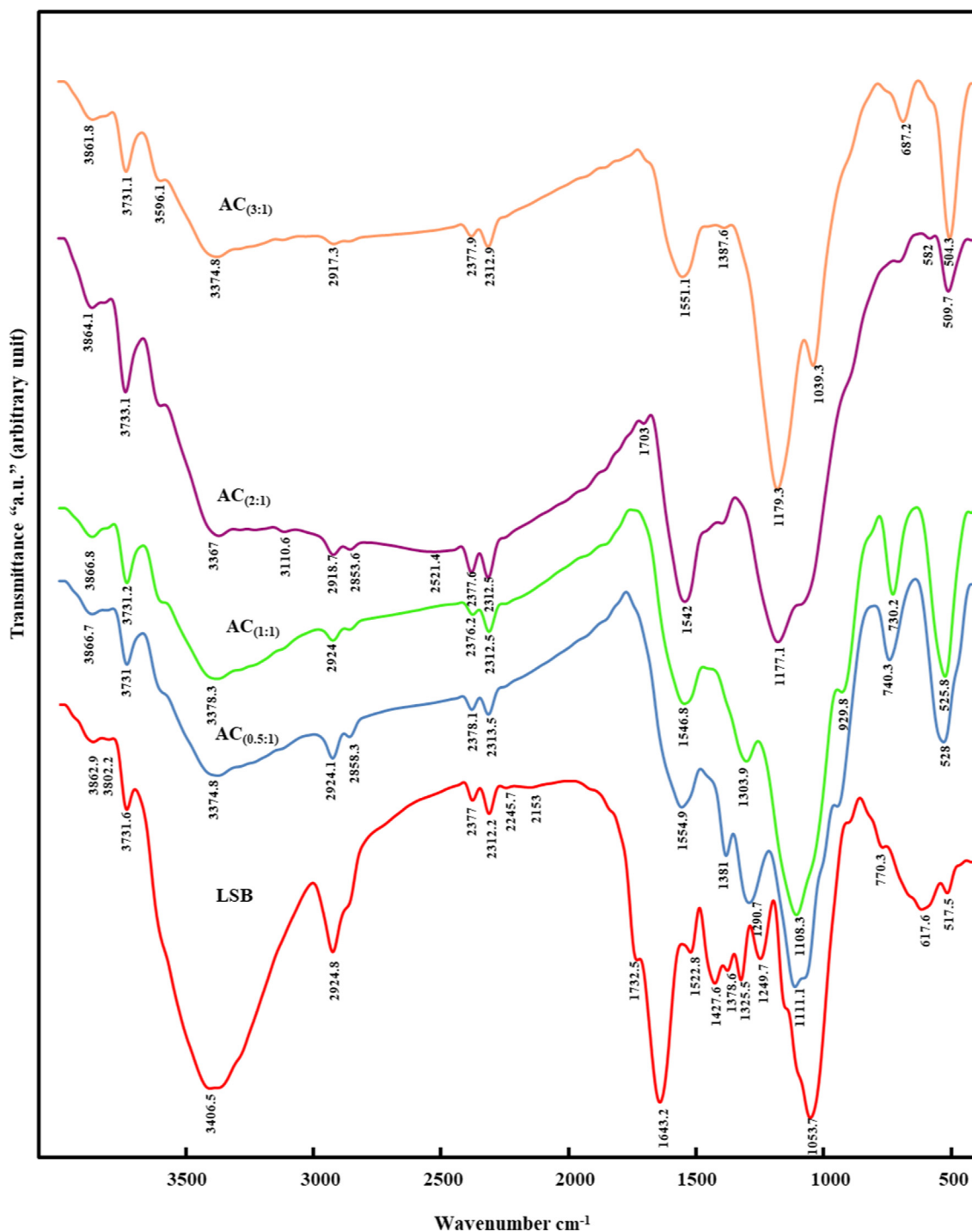
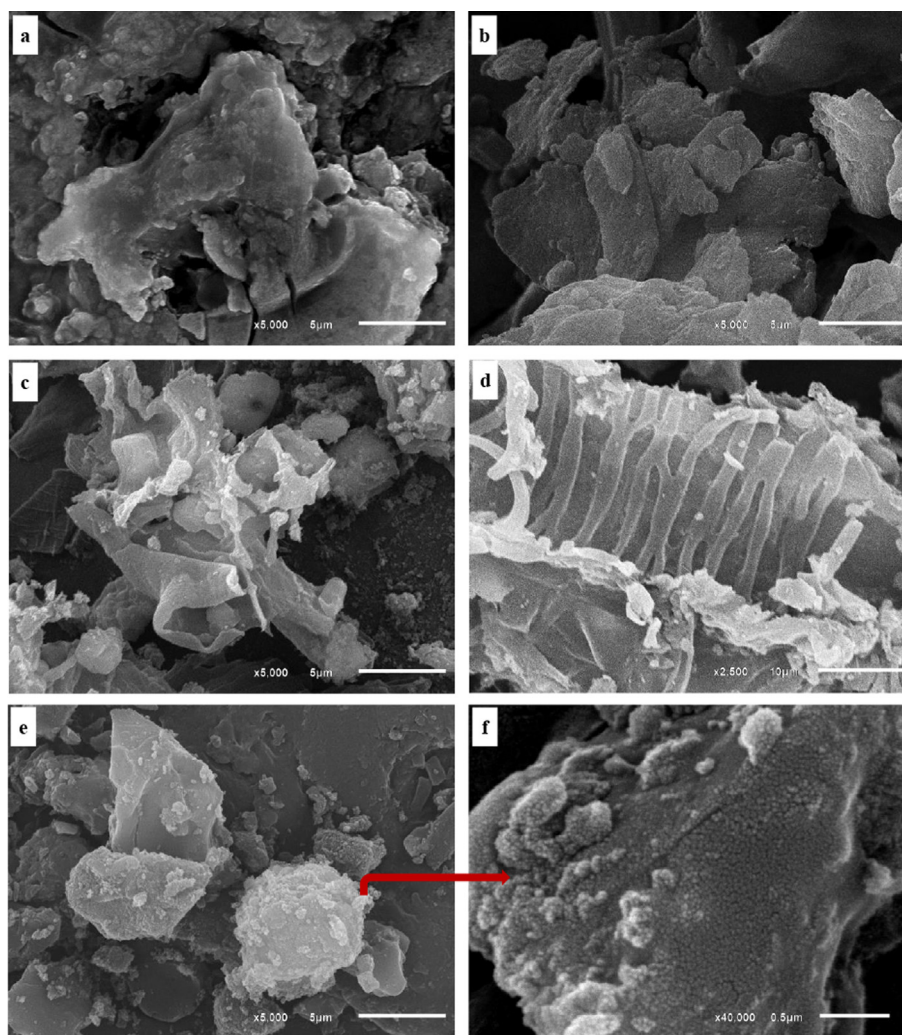


Fig. 3 FT-IR spectra of the synthesized ACs in comparison with the precursor LSB.

precursor LSB (Fernández et al., 2017). However, the logical disappearance of this phase in AC<sub>(2:1)</sub> & AC<sub>(3:1)</sub>, was ascribed to their approximate decomposition by the higher acid concentration during the activation process.

FT-IR spectra of the pristine LSB compared to those of their derivative ACs are given in Fig. 3. The LSB prevailing functional groups were reported at: 3406.5, 2924.8, 1634.2, and 1053.7  $\text{cm}^{-1}$  frequencies. The broad absorbance band at 3406.5  $\text{cm}^{-1}$  in the LSB spectra might be ascribed to the stretching mode of vibration of either O—H or N—H groups (Altundogan et al., 2007). In the derivative ACs, the amplitudes of N—H and/or O—H groups were gradually diminished with slight shifting to lower frequencies with increasing the applied acid concentration. In the meantime, the less intensified band at 2924.8  $\text{cm}^{-1}$  of the LSB that was ascribed to the stretching mode of C—H (alkenes) group of hemicellulose and cellulose (i.e., lignin polysaccharides) (Ghorbani et al., 2020; Malekbala et al., 2012), also was noticeably decreased in intensity with increasing the applied  $\text{H}_3\text{PO}_4$  concentration till almost complete fading in AC<sub>(1:3)</sub>. Such fading indicates the disintegration of the groups expressing the oxygenated

hydrocarbons (Shamsuddin et al., 2016). Matching with XRD outcomes, the feeble bands around 2300  $\text{cm}^{-1}$  of the precursor LSB, which were assigned to  $\text{CO}_2$  molecules in the stretching mode (Selim et al., 2018b; Tucureanu et al., 2016), were reduced in intensity with increasing the applied acid ratio in the derivatives ACs, especially AC<sub>(3:1)</sub>. Similarly, the C=C aromatic bond (Önal et al., 2007) and/or the asymmetric stretching modes of ( $-\text{COO}^-$ ) group (Malekbala et al., 2012) around 1634.2  $\text{cm}^{-1}$  in the LSB were vanished in the spectra of the derivative ACs. Conversely, the intensity of the C=C group in the stretching mode (Anisuzzaman et al., 2015) that emerged as a shoulder band at 1522.8  $\text{cm}^{-1}$  in the spectra of the precursor LSB, was amplified in the derivative ACs and shifted up to higher frequencies ( $>1540 \text{ cm}^{-1}$ ) (Tucureanu et al., 2016). This reflects a remarkable improvement in the aromatic characteristics of prepared ACs via the aliphatic component's transformation in the pristine LSB (Kumar and Jena, 2016). The 1053.7  $\text{cm}^{-1}$  intensified band in the LSB may be correlated with C—O stretching (Malekbala et al., 2012). With increasing the applied acid ratio, the C—O group (1053.7  $\text{cm}^{-1}$ ) was shifted up to higher frequencies in the

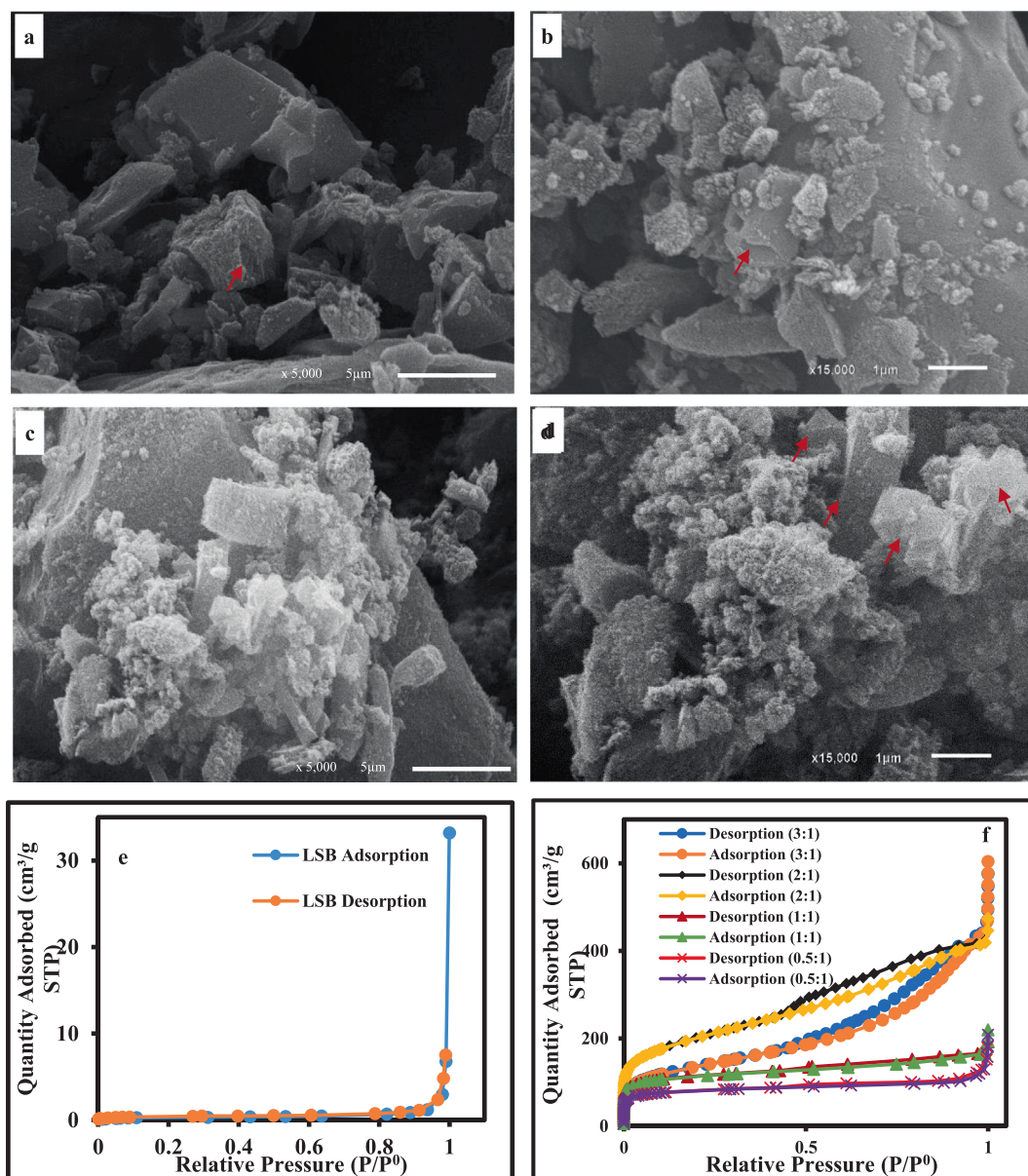


**Fig. 4** SEM images with different magnifications showing: (a-b) LSB with nodular crenulation as a reflection of rough surface; (c) AC (0.5:1) with rough surface and agglomerated spherical-like nanoparticles; (d) Survived texture of the LSB after acid activation to prepare AC (0.5:1) as a sign of in-complete activation; (e-f) Spherical-like nanoparticles of AC (1:1).

derivative ACs ( $\approx 1111$ - $1179\text{ cm}^{-1}$ ), indicating the coupling between the stretching mode of O—C group within the aromatic P—O—C linkages and hydrogen-bonded P=OOH groups from polyphosphates/and or phosphates (Han et al., 2020; Xu et al., 2014). Also the emergence of stretching vibration mode of P=O group in  $AC_{(0.5:1)}$  and  $AC_{(1:1)}$  at  $740.3$  and  $730.2\text{ cm}^{-1}$ , respectively, can be correlated to the applied  $H_3PO_4$  (Anisuzzaman et al., 2015). Moreover, the remarkable occurrence of the band at  $687.2\text{ cm}^{-1}$  only in  $AC_{(3:1)}$  and the bands at  $528$ ,  $525.8$ ,  $509.7$  and  $504.3\text{ cm}^{-1}$ , in all derivative ACs confirms the existence of out of plane deformation for the C—H that belong to benzene and alkenes derivatives with various grade of substitution (Canales-Flores and Prieto-García, 2020; Suganya and Senthil Kumar, 2018).

The SEM investigations displayed that both the precursor LSB and the derivatives ACs have rough and heterogenous surfaces crowded with nodular crenulation as a reflection of rough surface, with the preference of the derivatives (Fig. 4a-f & Fig. 5a-d). The porous nature of the surfaces in the as-synthesized ACs can be tied to the  $H_3PO_4$  evaporation during the carbonization process (Han et al., 2020; Kumar and Jena, 2016).

Concerning  $AC_{(0.5:1)}$ , the applied low acid concentration, resulted in immature activation process that contributed to the preservation of some survived texture of the precursor LSB (i.e. as a sign of incomplete activation process) side by side with a rough surface and agglomerated spherical-like nanoparticle as a reflection of a more surface heterogeneity



**Fig. 5** SEM images with different magnifications showing: (a,b) Spherical-like nanoparticles of AC (2:1) as a reflection of high amorphicity as well as grooves and cavities produced by the activating agent during the activation process of AC(2:1); (c-d) High graphitization degree with ideal prismatic crystals in AC(3:1) as a reflection of high crystallinity side by side with spherical-like nanoparticles indicating the remaining traces of the amorphous nature; (e) Nitrogen adsorption–desorption isotherms of LSB; (f) Nitrogen adsorption–desorption isotherms of the prepared ACs.



(Fig. 4c&d). Beyond 0.5:1 acid ratio (i.e., in AC<sub>(1:1& 2:1)</sub>), the primary texture of the LSB was entirely destroyed as a sign of a mature carbonization process (Fig. 4e-f & Fig. 5a-b). Therefore, the amount of the produced spherical nanoparticles upon the surfaces of these ACs was amplified. Some cavities and grooves were also created upon the precursor LSB surface by the activating agent during the activation process of AC (2:1) (Fig. 5b). Furthermore, the intensified occurrence of these nanoparticles upon their surfaces reflects the amorphicity degree of the prepared ACs, especially AC<sub>(2:1)</sub> in agreement with XRD data. However, the application of higher acid concentration (i.e. 3:1 ratio) improved the graphitization process of the organic carbon of the LSB to the limit that graphite crystals with the ideal prismatic habit (hexagonal shapes) were produced as a reflection of a high degree of crystallinity in AC<sub>(3:1)</sub> (Fig. 5c-d), matching with XRD data. Meanwhile, the occurrence of spherical-like nanoparticles in juxtaposition with the prismatic graphite crystals signifies that amorphous nature traces are still preserved in AC<sub>(3:1)</sub>.

The N<sub>2</sub> isotherms of LSB and their derivative ACs are illustrated in Fig. 5e-f. The precursor LSB displayed type III isotherm following the IUPAC classification (Thommes et al., 2015). This denotes that the investigated LSB has a macroporous habit with poorly connected semi-closed pore as was assured by the overlapping of the two branches of the given isotherm (Fig. 5e). The partial pore disconnection resulted in geometrical parameters with low quality (S<sub>BET</sub> = 1.5 m<sup>2</sup>/g, V<sub>t</sub> = 0.0107 cm<sup>3</sup>/g and D<sub>p</sub> = 28.7 nm).

On the contrary, the displayed isotherms of the derivative ACs were hybrid depending on the applied concentration of H<sub>3</sub>PO<sub>4</sub> acid (Fig. 5f). These various isotherms (from type II to IV) with respect to IUPAC classification (Kumar and Jena, 2016), denote microporous/mesoporous/macroporous characteristics of the produced ACs. These isotherms followed Type II in behavior with noticeable N<sub>2</sub> adsorption via the accessible micropores at the applied low relative pressure (P/P<sup>0</sup>) (Kumar and Jena, 2016). Conversely, these isotherms went along with type IV that displayed hysteresis loops of type H<sub>4</sub> at the applied P/P<sup>0</sup> of medium and high intensities, signifying monolayer/multilayer N<sub>2</sub> adsorption (Kumar and Jena, 2016). Furthermore, raising the acid concentration ratio from 0.5:1 to 2:1, was coupled with development in N<sub>2</sub> adsorption, signaling the gradual porosity improvement in the produced AC. In contrast, beyond 2:1 (i.e., 3:1), a noticeable decline in N<sub>2</sub> adsorption was recorded in line with the wall demolition among the neighboring pores. Therefore, the total porosity

and surface area of such active carbon were minimized (Sych et al., 2012).

Additionally, the progressive broadening of the hysteresis loops with increasing the applied acid assures these mesopores domination in the prepared AC. Likewise, the debility to attain the state of equilibrium of N<sub>2</sub> uptake by ACs, indicates the wide range of pore diameters.

The results of the geometrical parameters of the derivative ACs are compiled and compared with those of the precursor LSB (Table 3). It was displayed that the gradual increase in the utilized acid ratio from 0.5:1 to 3:1, resulted in a remarkable development in V<sub>t</sub> (0.01 to 0.68 cm<sup>3</sup>/g, orderly), indicating an important role of the activating agent in enhancing the ACs porosity via lignin structure destruction and the minimization of LSB cellulose (Tuli et al., 2020). For D<sub>p</sub>, the low H<sub>3</sub>PO<sub>4</sub> ratios (0.5:1 and 1:1) had an approximately equivalent impact; D<sub>p</sub> ≈ 2.5 nm. Nevertheless, further increase in acid ratios (2:1 and 3:1), contributed to a noticeable raise in the D<sub>p</sub> (3.7 and 5.7 nm, respectively).

Additionally, the S<sub>BET</sub> of all investigated ACs displayed a progressive enhancement from AC<sub>(0.5:1)</sub> to AC<sub>(2:1)</sub> (Table 3). Conversely, the S<sub>BET</sub> of the AC<sub>(3:1)</sub> declined to ≈ 480 m<sup>2</sup>/g although the high applied acid ratio. This S<sub>BET</sub> reduction can be tied with the improved crystallinity through an evolving of idioblastic hexagonal crystals of graphite in the AC<sub>(3:1)</sub> compared with the other ACs, matching with XRD and SEM outcomes.

### 3.2. Batch system experiments using aqueous solutions

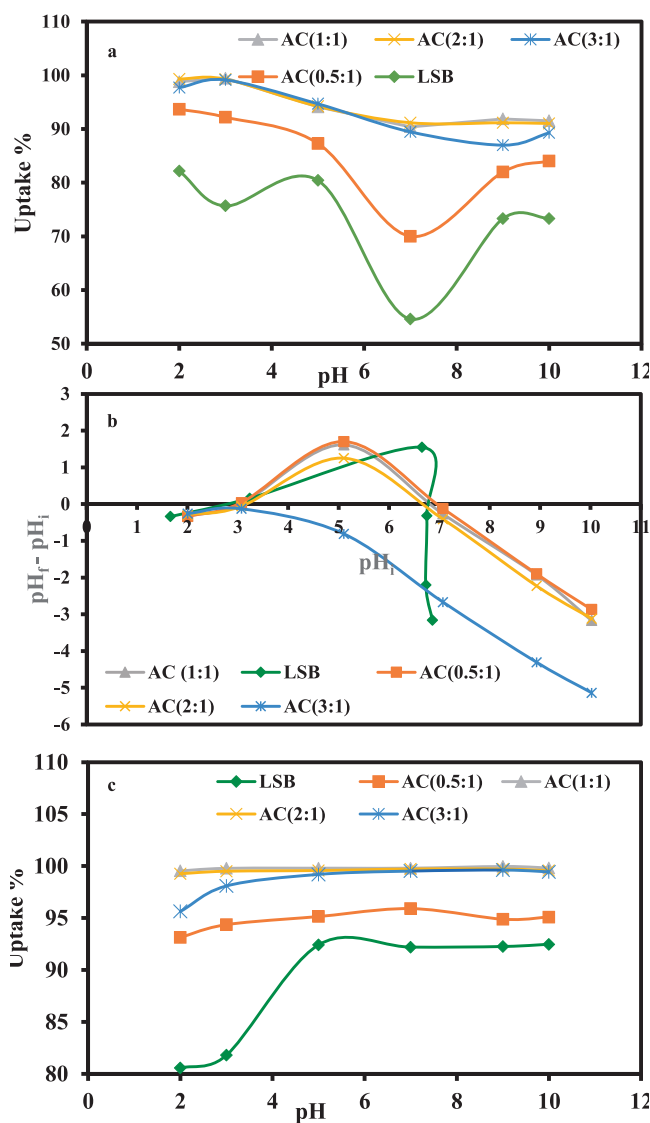
#### 3.2.1. Effect of pH

The MO remediation by the prepared ACs<sub>(0.5-1-3:1)</sub> and their precursor LSB is a pH-dependent process. Unlike the precursor LSB, ACs<sub>(1:1-3:1)</sub> displayed very high MO removal efficiency (R% > 97%) at pH 2.0–3.0 (Fig. 6a); the maximum R% was reached at pH 3.0 (>99%), in an agreement with preceding investigations (El-Sheikh et al., 2022b; Subbaiah and Kim, 2016; Zayed et al., 2018). On the contrary, AC<sub>(0.5:1)</sub> displayed a slightly high MO removal efficiency (R% > 92%) in both pH values (pH 2.0–3.0) in favor of the more acidic one. The exceptional sorption efficiency of the ACs for MO over LSB, was correlated with their higher geometrical parameters as was discussed before in the first technical report. Far of pH 5.0, MO sorption was slightly diminished, particularly in the basic medium, matching with the outcomes of pH<sub>PZC</sub> (point of zero charge) that was estimated following Singh

**Table 3** Geometrical parameters of the LSB compared to the derivative ACs obtained from the nitrogen adsorption/desorption isotherms.

Sample	Surface area (m <sup>2</sup> /g)			Pore volume (cm <sup>3</sup> /g)			Average pore diameter (nm)
	BET (S <sub>BET</sub> )	Mesopores (S <sub>Meso</sub> )	Micropores (S <sub>Micro</sub> )	Total pore volume (V <sub>t</sub> )	Meso-pore volume (V <sub>Meso</sub> )	Micro-pore volume (V <sub>Micro</sub> )	
LSB	1.50	0.54	0.96	0.01	0.004	0.006	28.70
0.5:1	300.30	120.1	180.2	0.20	0.08	0.12	2.68
1:1	416.80	126.4	290.4	0.26	0.08	0.18	2.48
2:1	700.70	440.2	260.5	0.65	0.41	0.24	3.69
3:1	480.60	356.2	124.4	0.68	0.50	0.18	5.70

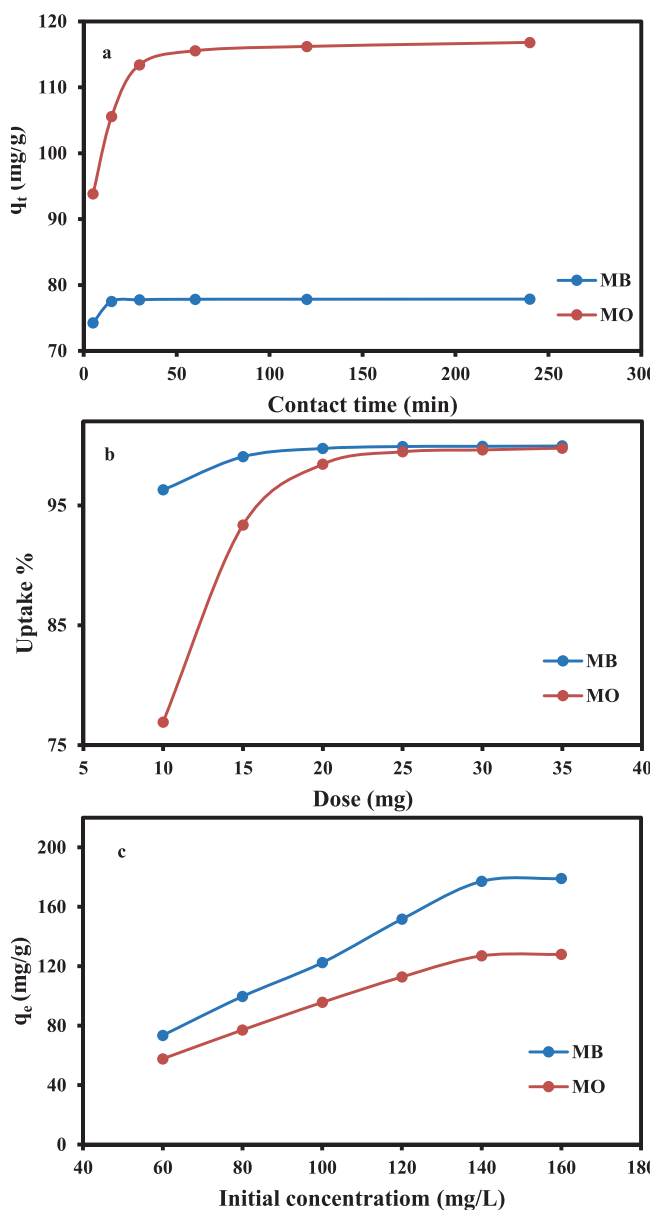
et al. protocol (Singh et al., 2015). Such outcomes demonstrated that the ACs ( $_{(0.5:1-2:1)}$ ) and its LSB surfaces are consistently negative except between  $\approx$  pH 3.1 to 6.8 at which their surface has positive charges ( $\text{pH}_{\text{PZC}}$  of LSB  $\approx$  2.9 and 6.75,  $\text{AC}_{(0.5:1)}$   $\approx$  3.1 and 6.9,  $\text{AC}_{(1:1)}$   $\approx$  3.1 and 6.9,  $\text{AC}_{(2:1)}$   $\approx$  3.2 and 6.7) (Fig. 6b). On the contrary,  $\text{AC}_{(3:1)}$ , revealed negative charge along the investigated pH interval. Specifically, the electrostatic interactions between the binding sites of the studied sorbents and the negative sulfonate group ( $-\text{SO}_3^-$ ) of MO ions in solution were facilitated by the higher degree of ionization of MO ( $\text{pK}_a = 3.46$ ; (Asuha et al., 2010; Umpuch and Sakaew, 2013)) and the protonation of the ACs and LSB surfaces at pH 3.0. In this situation, hydrogen ions function as bridging ligands between the MO anions and the targeted adsorbent surfaces during the protonation process. On the contrary, the presence of competitive  $\text{OH}^-$  ions in the solution caused deprotonation of sorbent's surfaces, generating repulsive interactions against MO anions and reducing its uptake



**Fig. 6** Plots of AC ( $_{(0.5:1- 3:1)}$ ) compared to their precursor LSB showing: (a) Effect of pH on MO uptake; (b) Zero charge points; (c) Effect of pH on MB uptake.

(Mohammadi et al., 2011). As a result, pH 3.0 was chosen as the experimental pH for the following experimental work.

Although electrostatic contact is a major factor, additional hydrophobic forces (hydrogen bonding, H-bonding) may also play a significant role in the sorption of MO by the targeted adsorbents (Tran et al., 2017a; Zayed et al., 2020). The hydrophobicity of graphite and/or organic matter contents of ACs and LSBs is likely to be the source of these forces (Akhair et al., 2018; Yee et al., 2009). Two types of hydrogen bonding interactions have been identified: 1) dipole-dipole and 2) Yoshida (Tran et al., 2017a; Zayed et al., 2020). The interaction among surface hydroxyl groups of the investigated sorbents and the aromatic rings of the MO, denotes the 2nd sort of H-bonding (Tran et al., 2017a; Zayed et al., 2020). Whereas the interaction that connects the MO's nitrogen /oxygen atoms



**Fig. 7** Plots showing: (a) Effect of contact time; (b) Effect of dose; (c) Effect of initial concentration on MO & MB uptake by the applied  $\text{AC}_{(2:1)}$ .

(H-acceptor) to the accessible hydrogen atoms (H-donor) of the sorbent's hydroxyl groups, signifies the 1st sort of H-bonding (Tran et al., 2017a; Zayed et al., 2020). The significant sorption efficiency of MO by the targeted adsorbents at pH 9.0–10.0 (73.3 to 91.9%), despite the presence of OH<sup>-</sup> as competing ions in the solution, confirmed the participation of H-bonding process.

Similarly, the initial pH played a critical role in MB uptake by the addressed adsorbents from the aqueous solution (Fig. 6c). Unlike the parental LSB, the prepared ACs revealed high removal capacity (R % = 93 to 99.96%) in pH range from 3.0 to 10.0; equilibrium was reached at pH 9.0 (R% > 99) for all the investigated ACs (1:1-3:1), except for AC(0.5:1) that displayed only R% = 94.8%. Far away from pH 9.0, MB removal by the addressed adsorbents presented no considerable increase in the R%.

The high MB uptake efficiency at pH 2.0, 3.0, and 5.0 (> 93%) despite the intense competition with H<sup>+</sup> ions, implies that electrostatic forces (i.e non-hydrophobic forces) cannot be counted as the main mechanism for MB remediation by the regraded sorbents; other forces can be counted as a driving force for MB adsorption (Tran et al., 2017b).

The high MB uptake capacity by the regarded adsorbents at basic mediums, nominated pH 9.0 for executing the following experimental work.

Based on the previously discussed geometrical parameters and the pH experiments' results, AC<sub>(2:1)</sub> was selected for remediation of both MB and MO in the succeeding experimental parameters.

### 3.2.2. Effect of contact time

Studies conducted at various equilibrium times demonstrated that the adsorption of MO ions by AC<sub>(2:1)</sub> was very fast in the time interval from 5 to 30 min, with  $q_t$  ranging from 93.83 to 113.42 mg/g, respectively (Fig. 7a). This can be correlated with the high surface area of the regarded sorbent with plentiful available binding sites (Saleh et al., 2014). However, equilibrium was attained at 60 min, expressing the chemical character of the adsorption process of MO ions by the regarded sorbent (Cheah et al., 2013; Chen et al., 2010). After 60 min, no appreciable  $q_t$  was achieved (115.54–116.8 mg/g).

Similarly, MB uptake (Fig. 7a) by AC<sub>(2:1)</sub> was very speedy during retention times between 5 and 15 min (74.28 and 77.51 mg/g, respectively) indicating that the adsorption process is a time-controlled one (Kim et al., 2016). This was linked to the abundance of free binding sites on the AC surface, which

**Table 4** Adsorption kinetics and isotherm models for MO & MB uptake by AC<sub>(2:1)</sub> adsorbent.

Kinetic/ isotherm Model	Linear form	Parameters	Refs.
<b>Pseudo- second-order</b>	$\frac{t}{q_t} = \frac{1}{k_2 - q_e^2} + \frac{t}{q_e}$	$q_t$ (mg/g): removed amount of MO & MB at time t. $q_e$ (mg/g): equilibrium adsorption uptake. $k_2$ (g/mg min): rate constant of the second-order adsorption. $q_e^{(calc.)} = 1/slope$ $k_2 = (slope)^2 / intercept$	(Ho and McKay, 1999)
<b>Intra-particle diffusion</b>	$q_t = k_p t^{1/2} + C$	$q_t$ (mg/g): removed amount of MO & MB at time t. $K_p$ (mg/g min <sup>0.5</sup> ): intra-particle diffusion rate constant. $C$ (mg/g): intercept of the line which reflects the thickness of the boundary layer. $k_p = slope$ $C = intercept$	(Weber and Morris, 1962)
<b>Langmuir</b>	$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}}$	$C_e$ (mg/L): equilibrium concentration of the resting MO & MB in the solution $q_e$ (mg/g): removed amount of MO & MB at equilibrium. $q_{max}$ (mg/g): maximum adsorption capacity $K_L$ (L/mg): Langmuir constant $q_{max} = 1/slope$ $K_L = slope / intercept$	(Langmuir, 1916)
	$R_L = 1 / (1 + K_L C_0)$ $R_L > 1$ (unfavorable adsorption) $R_L = 1$ (linear adsorption) $(0 < RL < 1)$ (favorable adsorption) $R_L = 0$ (irreversible adsorption)	$R_L$ : Equilibrium parameter of Langmuir equation. $C_0$ : Initial MB & MO concentration.	(Weber and Chakravo, 1974)
<b>Freundlich</b>	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	$C_e$ (mg/L): equilibrium concentration of the resting MO & MB in the solution $q_e$ (mg/g): removed amount of MO & MB at equilibrium. $K_F$ (mg/g)*L/mg) <sup>(1/n)</sup> : MO & MB adsorption capacity. $n$ : heterogeneity factor. $K_F = 10^{intercept}$ $1/n = slope$	(Freundlich, 1906)

were available to interact with MB ions (Agarwal et al., 2016). After 15 min, there was no discernible increase in the MB adsorption rate ( $q_t$  77.8 mg/g), indicating that equilibrium had been reached. Rapid equilibrium suggests the chemical basis of MB adsorption and nominates  $AC_{(2:1)}$  as a suitable adsorbent for MB adsorption.

### 3.2.3. Effect of adsorbent dose

Removing MO from a solution with an initial concentration of 120 mg/L using variable masses (10 to 35 mg) of  $AC_{(2:1)}$  was analyzed deeply (Fig. 7b). By raising the mass of the regarded AC from 10 mg to 20 mg, the MO elimination capacity rose from 76.9% to 98.5%. However, the MO adsorption capacity increased only marginally (99.8%) when a mass of > 20 mg was used. This logical progression leading to equilibrium can be unrelated to the number of binding sites (O- and N-containing groups) on the AC's surface (Mokhtari et al., 2016; Saleh et al., 2014).

As well, the R% of MB at various masses of the addressed AC (10 to 35 mg) displayed that equilibrium state (R% > 99%) was attained by increasing the applied dose beyond 10 mg (Fig. 7b). This can be justified by the occurrence of bountiful unoccupied active sites upon the AC surface (Mokhtari et al., 2016; Saleh et al., 2014).

So the optimum masses of  $AC_{(2:1)}$  application in the adsorption of MB and MO was 15 and 20 mg, respectively.

### 3.2.4. Effect of initial concentration

The progressive raise in the initial concentration of applied MO (60–160 mg/L) was accompanied by an improvement in  $q_e$  (mg/g) from 57.7 to 128.02 mg/g (Fig. 7c). This can be accounted by the developing rate at which MO ions collide with the AC's sites. In addition, the elevated mass gradient that propelled the MO ions to the AC surface was the source of the sorption improvement (Shiue et al., 2012).

Likewise, the development of MB concentration from 60 to 160 mg/L, enhanced the attained  $q_e$  (mg/g) per unit mass of the regarded  $AC_{(2:1)}$  till equilibrium (Fig. 7c).

### 3.2.5. Isotherm studies

The linear form of two of the widely used isotherm models (Langmuir and Freundlich models) was employed to elucidate the interactive nature between the adsorbate (MO & MB) and  $AC_{(2:1)}$  (Freundlich, 1906; Langmuir, 1916) and to get helpful information about the surface properties of the regarded sorbent and their affinity to the probed dyes. Tables 4 and 5 display these linear equations and their estimated parameters, respectively. Therefore, the plots of  $C_e/q_e$  vs.  $C_e$  and  $\log q_e$

vs.  $\log C_e$ , were employed to estimate the Langmuir and Freundlich parameters, orderly (Fig. 8).

The Langmuir isotherm presupposes that the adsorption process occurs at discrete isoenergetic binding sites on the sorbent surface in form of a monolayer (Chen et al., 2010; Hameed, 2009). Oppositely, the Freundlich isotherm assumes the adsorbate will be compiled as several layers (a heterogeneous adsorption process) on the sorbent surface (Selim et al., 2018a).

Adsorption data of the probed dyes by AC were best characterized by Langmuir isotherm, as was evident from the determination coefficient results of the two applied models (i.e.,  $R^2 = 0.9997$  and  $0.9992$  for MO and MB, respectively, using Langmuir equation) (Table 5). As a result, the adsorbed MO and MB ions formed monolayers on the negatively and positively charged isoenergetic sites upon the AC surface

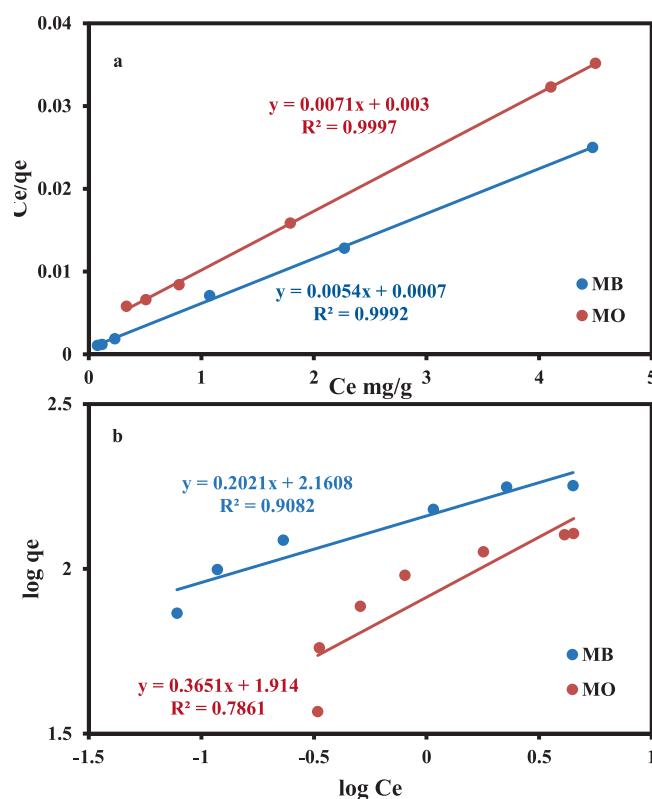


Fig. 8 Isotherm linear plots for MB and MO removal by  $AC_{(2:1)}$  using: (a) Langmuir; (b) Freundlich equations.

Table 5 The isotherm parameters of the MO & MB adsorption by  $AC_{(2:1)}$  adsorbent.

Initial concentration (60–140 mg/L)	Isotherm Model					
	Langmuir			Freundlich		
	Parameters			Parameters		
	$q_{max}$ (mg/g)	$K_L$ (L/mg)	$R^2$	$1/n$	$K_F$ (mg/g)*L/mg <sup>(1/n)</sup>	$R^2$
MB	185.2	7.714	0.9992	0.2021	144.8105	0.9082
MO	140.8	2.367	0.9997	0.3651	82.035	0.7861

(Chen et al., 2010; Jawad et al., 2019b; Jawad et al., 2019c). The Langmuir equilibrium parameter  $R_L$  for both dyes, was also determined using the formula presented in Table 5. The values of  $R_L$  for MB and MO ranged from 0.0008 to 0.0022 and 0.003 to 0.011, orderly (positive,  $0 < R_L < 1$ ). These obtained values indicate that Langmuir could be utilized to adequately present the adsorption data for both dyes via AC<sub>(2:1)</sub>.

However, the discrepancy in  $q_{max}$  (the maximum adsorption capacity) of MO and MB ions (140.80 and 185.20 mg/g, orderly) endorses the larger played role of the negative active site than the positive ones (Cunha et al., 2020) and hence the more considerable affinity for MB compared to MO (i.e., the overall number of acidic sites is larger than the basic ones matching with other previous studies). So, the prepared AC<sub>(2:1)</sub> can be classified as an effective sorbent for such dye species.

A comparison of the  $q_{max}$  of MO and MB remediation by the addressed AC<sub>(2:1)</sub> with other adsorbents showed the superiority of the current adsorbent over the other investigated natural, modified, and synthetic ones (Table 6).

### 3.2.6. Kinetic studies

The linear expression of the PSO “pseudo-2nd-order” and IPD “inter-particle diffusion” equations were employed to elucidate the kinetics of MB & MO sorption by AC sorbent (Ho and McKay, 1999) (Table 4). Also, the parameters of these models were estimated and tabulated in Table 7.

The MO and MB sorption process by the AC<sub>(2:1)</sub> was illustrate-well by PSO equation (Fig. 9a). This implies that chemisorption could be the rate-governing step of their removal (Hasanzadeh et al., 2020; Jawad et al., 2019a; Norouzi et al., 2018) as was assured by the obtained  $R^2$  (one for both dyes) (Mohamed et al., 2019; Wang et al., 2011). As well, this was confirmed through the close matching between the calculated ( $q_e^{cal.} = 78.125$  and  $117.65$  mg/g, for MB and MO, orderly) and the experimental  $q_e$  ( $q_e^{exp.} = 77.51$  and  $115.54$  mg/g, for MB and MO, orderly) (Table 7).

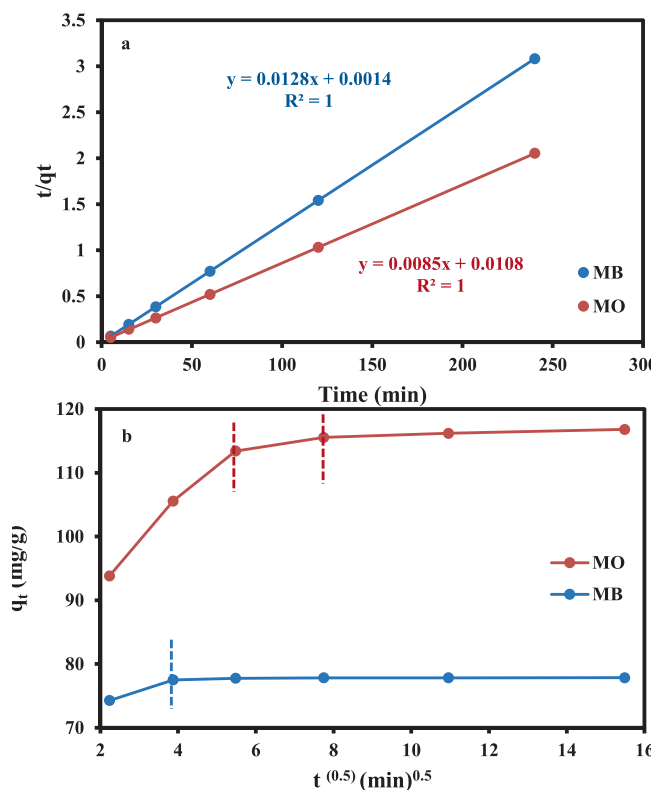
Furthermore, the IPD equation that was graphically displayed through  $q_t$  vs.  $t^{0.5}$  plotting, gave a multistage linear plot deviating away from the origin; 2 and 3 stages for MB and MO, were recorded (Fig. 9b). These multilinear plots denote that MB and MO sorption by the AC was not mainly illus-

**Table 6** Adsorption capacity for MO and MB by some natural, modified and synthetic materials in comparison with the AC<sub>(2:1)</sub> of the present study:  $q_{max}$  obtained from the Langmuir constant.

Adsorbent	Adsorption capacity	Adsorption capacity	Reference
	$q_{max}$ (mg/g) of MO	$q_{max}$ (mg/g) of MB	
Cellulose/clay composite hydrogel	–	277	(Wang et al. 2019b)
Zeolite/chitosan composite	–	199	(Khanday et al. 2017)
Sericin/ $\beta$ -cyclodextrin/PVA composite	–	261	(Zhao et al. 2015)
Halloysite-Cyclodextrin Nanosponges	–	226	(Massaro et al. 2017)
Chitosan/polyvinyl alcohol/zeolite	153	–	(Habiba et al. 2018)
Cotton fiber	–	113	(Xiong et al. 2014)
Modified pine sawdust.	–	84	(Zhang et al. 2015)
sawdust	–	–	–
Fe-MIL-88NH2	–	15.99	(Fu et al. 2021)
ZIF-8@SiO2@MnFe2O4	78.12	–	(Abdi et al. 2019)
Fe-MIL-88NH2	58.72	–	(Fu et al. 2021)
Poly(N-isopropyl acrylamide-coitaconic acid)/crosslinked with OVPOSS	–	130	(Eftekhari-Sis et al. 2018)
Carboxymethyl cellulose coated Fe3O4@SiO2 magnetic nanoparticles	–	17.5	(Zirak et al. 2018)
$\beta$ -CD-SNHS	–	99.22	(Ebadi and Rafati 2015)
Co3O4 nanocube-doped polyaniline	107	–	(Shahabuddin et al. 2016)
Modified PAN	99.15	–	(Cháuque et al. 2017)
Activated clay	16.78	–	(Ma et al., 2012)
Maghemite/chitosan nano-composite films	29.41	–	(Jiang et al., 2012)
Bentonite	33.8	–	(Leodopoulos et al., 2012)
Organic matter rich clays (OMRC)	41.67	–	Zayed et al., 2018
Calcinated organic matter rich clays (COMRC)	34.48	–	Zayed et al., 2018
Modified wheat straw	50.4	–	(Su et al., 2014)
Modified coffee waste	62.5	–	(Lafi and Hafiane, 2016)
Mesoporous carbon CMK-3	294.1	–	Mohammadi et al., 2011
Powdered activated carbon modified by HNO <sub>3</sub>	384.62	–	(Do et al., 2011)
Activated carbon/Fe <sub>3</sub> O <sub>4</sub> nanoparticle composites (10Fe3O4/PAC-HNO3)	303.03	–	(Do et al., 2011)
Ephedra strobilacea char (ESC)	–	31.055	Agarwal et al.(2016)
Phosphoric acid modified Ephedra strobilacea char (ESP)	–	21.88	Agarwal et al.(2016)
Zinc chloride modified Ephedra strobilacea char (ESZ)	–	37.174	Agarwal et al.(2016)
Alginate/almond peanut biocomposite	–	22.8	Erfani and Javanbakht (2018)
AC <sub>(2:1)</sub>	140.8	185.2	Current study

**Table 7** The kinetic parameters of the MO & MB adsorption by AC adsorbent.

Adsorbent	Dye	Initial concentration (mg/L)	$q_e^{(exp.)}$ (mg/g)	Kinetic Model					
				Pseudo-second order			Intra-particle diffusion		
				Parameters			Parameters		
AC (2:1)				$k_2$ (g/mg min)	$q_e^{(Calc.)}$ (mg/g)	$R^2$	$K_p$ (mg/g min <sup>0.5</sup> )	$C$ (mg/g)	$R^2$
	MB	80	77.51	0.117	78.125	1	1.9714	69.875	1
	MO	120	115.54	0.0067	117.65	1	0.9344	108.3	1

**Fig. 9** Linear plots for MB and MO remediation by AC<sub>(2:1)</sub> using: (a) Pseudo-second order; (b) Intra-particle diffusion equations.

trated by IDP but several types of diffusion may be intervening (Abdulhameed et al., 2019; Gusain et al., 2016; Selim et al., 2018a; Zayed et al., 2017).

The steep portions (1st stage) denote that exterior mass transfer and /or boundary diffusion layer could be the inspiring step of MO ions adsorption by AC binding sites (Naiya et al., 2009; Wang and Zhu, 2006). Such portion (1st stage) is missing in MB plot as a sign of rapid accomplishment of the external surface adsorption (Suganya and Senthil Kumar, 2018). The quiet-slope portions (2nd stage) for the regarded dyes, point to steady ions sorption by AC<sub>(2:1)</sub>; IPD was the main mechanism (Agarwal et al., 2016). So, the 2nd stage was used to estimate the  $C$  and  $K_p$  constants (Chen et al., 2010) as depicted in Table 7. The plateau portions (3rd stage) reflect the attained equilibrium state with almost fixed rate of ions sorption by the regarded AC.

As well, the high  $C$  values (69.875 and 108.3 mg/g for MB & MO, orderly) validated that their ions removal by AC<sub>(2:1)</sub> was not totally defined by IPD, but several diffusion types may be incorporated (Abdulhameed et al., 2019; Gusain et al., 2016; Selim et al., 2018a; Zayed et al., 2017). Such constant values reflect the effective participation of the AC surface in MO removal better than in MB.

#### 4. Conclusion

The outputs of the current work were compiled in the following points:

- The environment-polluting LSB wastes accumulated annually after sugar beet crop harvesting, were successfully transformed into sustainable/high market value ACs through a simplified thermochemical activation process.
- The activation process of the produced ACs was improved by applying different ratios of robust activating agents (0.5:1, 1:1, 2:1, and 3:1 of H<sub>3</sub>PO<sub>4</sub>/LSB) that served as a pyrolytic decomposer of the LSB during the calcination process (550 °C/2h), impeding the ash formation.
- The highest degree of amorphicity and  $S_{BET}$  (700.7 m<sup>2</sup>/g) nominated AC<sub>(2:1)</sub> for MO and MB remediation from synthetic solutions.
- The sorption process MO & MB by the prepared AC<sub>(2:1)</sub> was a pH- and time-reliant procedure; the maximum removal capacity was attained at pH 3.0 & 9.0 and equilibrium was reached at 60, and 15 min, orderly.
- The kinetics of MO and MB sorption process by the AC<sub>(2:1)</sub>, were illustrated-well by the PSO model following the attained high  $R^2 = 1$  and the approximate agreement among the experimental and theoretical  $q_e$  values.
- The IDP was not the only inspiring step in the sorption process of MO and MB dyes by the prepared AC<sub>(2:1)</sub>, but other diffusion styles may be incorporated.
- The isotherm study revealed that the sorption procedure of the investigated dyes was explained well by Langmuir equation, confirming the separate accumulation of each of these contaminant's ions as a homogeneous monolayer upon the surface of the addressed activated carbon via isoenergetic N- and O-bearing binding sites.
- Finally, the synthesized AC<sub>(2:1)</sub> is categorized as a superior/ eco-friendly adsorbent for both thiazine and azo dyes with some privilege for the former.

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