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The Perlite-calcium Alginate-activated Carbon Composite as an Efficient Adsorbent for the Removal of Dyes from Aqueous Solutions

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To remove dyes from wastewater, the perlite-calcium alginate-activated carbon (PCA) composite was prepared by a simple method. This composite was characterized by FTIR, XRD, SEM and BET techniques. A high capacity of PCA was observed for the adsorption of some dyes such as methylene blue (MB) and methyl orange (MO) from aqueous solutions 1111 and 909 mg g^{-1}. The best results were achieved at pHs 3 and 8, dyes initial doses 8 and 10 ppm, adsorbent doses 0.008 and 0.01, time 60 min and temperature 15-20 °C for MO and MB. The adsorption of MB and MO on the as-prepared PCA was matched by pseudo-second order model and corresponded to the Langmuir isotherm. Under optimum adsorption conditions, the yield of adsorption was obtained for MB and MO. Results indicated that PCA can be a good candidate for adsorption of dyes. The proposed green chemistry-based preparation method is simple, economical, and more reusable compared to the individual application of primary materials.

Keywords: Alginate, Perlite, Activated carbon, Methylene blue, Methyl orange

INTTRODUCTION

An important turning point in human history has been the industrial revolution. However, it has disadvantages such as environmental pollution [1]. The environmental safety can be compromised by the waste of the textile, food and pharmaceutical manufactures, which can affect the weather, water and land. The pollution of drinking water, rivers and seas can change the quality of human life. Industries can release the pollutants such as toxic dyes, which have been categorized by Central Pollution Control Board (CPCB) [2]. The generated dyes cannot be separated easily and can remain in water for a long time, posing potential life-threatening risks for human health [3]. The skin allergy and irritation are some effects of wastewater pollution, due to the development of industries. Synthetic dyes display properties such as stability and resistance to degradation [4-6].

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The output of dye manufacturing industries generates wastewater, which has aroused people's concern regarding the environmental safety. The recycling from the manufacturing sectors and the textile industries pours into the seas and rivers, altering the biochemical stability of the surroundings [7]. The removal of chromophore groups including nitrogen stable structures is a difficult task which is considered as a serious challenge. It is noteworthy that some of the mentioned technologies can produce harmful residues.

Over the last decade, the removal of pigments from the waste has been fully considered. There are several procedures to remove effluents including advanced oxidation [8-9], coagulation [10] and adsorption [11] techniques. However, some of these methods are expensive, complicated, and have low yields. One of the most prevalent and important techniques is the adsorption of organic pollutants from wastewater. Nowadays, several procedures can be applied to adsorb the wastes from agriculture and different industries such as silicate, clay, and solid wastes [12-15].

The adsorption activity of the carbon family is well established. They have shown special properties thanks to having a unique structure [16-20]. One of the earliest methods of adsorption is application of the activated carbon [21,22] As an instance, quinoline can be removed by sulfuric acid-treated activated carbon as the adsorbent [23]. In an assessment, the removal of basic dye was studied using ZnS:Cu nanoparticles loaded on activated carbon [24]. Moreover, the adsorption of methylene blue has been investigated using activated carbon, from coconut shell waste [25]. In another research, Fe_3O_4 NPs@AC@$C_4H_8SO_3H$ was employed for the adsorption of heavy metal ions from aqueous solutions [26]. The modified activated carbon by polyols can be applied for the removal of boron-polluted waters [27]. The cationic surfactants on activated carbons have demonstrated capabilities and potentials for the purification of water [28]. These low-cost adsorbents possess a high specific surface area, but their production is costly.

Among natural compounds, clay minerals are a good candidate for adsorption, thanks to their simple procedure, low cost, high porosity, and being eco-friendly. The perlite, as a mineral compound, can be used for removal of the organic pollutants, because of its special mixture containing SiO_2 and Al_2O_3 as a porous structure [29]. The expanded perlite can be used as an adsorbent for thorium [30], cetyltrimethylammonium bromide (CTAB) [31] and cationic polyacrylamide (C-PAM) [32]. The magnetic $ZnFe_2O_4$/ZnO/perlite can be applied for the removal of methylene blue (MB) and 4-nitrophenol (4-NP) [33]. The humic acid can be adsorbed by perlite granules/nano TiO_2 particles [34]. However, the high efficiency of the perlite for removal of pollutants might be limited by its structure due to low capacity, difficult reusability, and poor interaction with organic pollutants [35,36].

The brown algae can produce particular polysaccharides such as alginates. This compound is composed of α-L-guluronic and β-D-mannuronic acids [37]. Calcium alginate, possessing a 3D network structure, displays unique properties such as non-toxicity and being eco-friendly. Alginate has many applications such as ionotropic gelation or being used as thickening agent that can be coupled with other structures especially carbon class [38,39] and nanoparticles [40]. Calcium alginate beads can be modified by many materials to obtain the required properties for water purification [41]. Different physical and chemical methods can be employed for surface modification of the adsorbent to achieve a high yield. These strategies have prominent effects for removal of the organic pollutants [42].

Typically, in the present research, in order to obtain the best results, three materials including the activated carbon, alginate and perlite were combined together, since low efficiency, difficult reusability, poor adsorption of the organic materials and the high cost were achieved when they were used individually. A key problem with activated carbon is the cost of the raw material, due to its preparation method [21]. In addition, the application of clay minerals has serious problems including low surface area, difficult recovering process with low efficiency and poor adsorption of the organic molecules [29].

In this work, the following objectives were investigated: 1- preparation of perlite-calcium alginate–activated carbon composite (PCA); 2-characterization of the proposed composite using FTIR, XRD, SEM and BET; 3- the study of methyl orange (MO) and methylene blue (MB) adsorption on PCA.

The limitation of perlite, activated carbon and calcium alginate including poor interaction of organic compounds, expensive preparation of composite for adsorption can be restricted by combining them. To overcome these problems, this idea can be used effectively toward the individual application of adsorbents, due to simple and cheap preparation of composite, application for dyes, high yield and easy regeneration and that the preparation method needs a lower amount of activated carbon compared to its individual use. Therefore, the combination of these materials would be a good alternative to achieve an efficient composite for adsorption of dyes.

EXPERIMENTAL

Materials and Instruments

Perlite was provided from Khorasan Razavi mine, Iran. Sodium alginate, calcium chloride ($CaCl_2$), sodium hydroxide (NaOH), hydrochloric acid (HCl), methylene blue (cationic dye, $C_{16}H_{18}ClN_3S$, 319.85 g mol^{-1}, Fig. 1a), methyl orange, anionic dye $C_{14}H_{14}N_3NaO_3S$, 327.33 g mol^{-1}, Fig. 1b) and activated carbon were

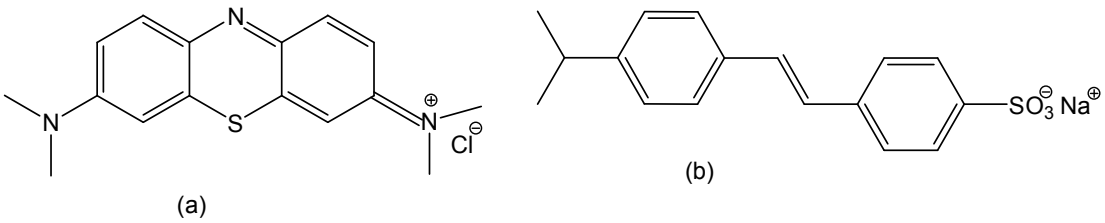

Fig. 1. Chemical structures of (a) methylene blue and (b) methyl orange.

purchased from Aldrich and Merck Chemical Companies, Germany.

FTIR spectra were obtained by Shimadzu 8400s spectrometer. Powder XRD patterns were recorded by Stadip (STOE, Germany) using Cu-Ka radiation at wavelength of 1.54 Å. Field-emission scanning electron microscope (FESEM) images were acquired using TESCAN field-emission scanning electron microscope (Czech). The nitrogen adsorption-desorption isotherms of PCA were measured by Belsorp-Mini II and Bel Prep VAC II (BEL, Japan). The ultraviolet-visible spectra were obtained by Dynamic-DB-20.

Preparation of Neat Perlite Powder

The neat perlite was prepared by mixing 5 g of perlite with 50 ml of ethanol and methanol for 12 h, followed by washing with deionized water. 5 N NaOH was subsequently added to this mixture for 30 min and the obtained precipitate was filtered and dried at 100 °C [43].

Preparation of the Perlite-calcium Alginate-Activated Carbon Composite

1 g of perlite and 1 g of activated carbon were added to 2% sodium alginate. This solution was stirred for 12 h under dark conditions. Next, 2% (w/v) calcium chloride was added to the mixture slowly. The perlite-calcium alginate-activated carbon composite formation was achieved by addition of calcium chloride. The resulting mixture was filtered and dried.

Adsorption Batch Experiments

The adsorption of MB and MO were assessed using a batch equilibrium method. The initial doses of MB and MO were determined in water (15 ml). The solution parameters including pH (2-12), initial doses of MB and MO (2-22 ppm), adsorbent doses, time (15 min-6 h) and temperature (15-45 °C) were evaluated in an aqueous solution. After adsorption-desorption equilibrium was achieved, the resulting suspensions were centrifuged to remove the adsorbent and the final doses were determined using UV-Vis spectrophotometer.

The point of zero charge (pHpzc) was determined by Auta and Hameed method [44]. The initial pH (pH_i) of aqueous solutions (200 ml) was adjusted to a pH range of 2-12, and 0.2 g PCA was added and stirred for 48 h at 30 °C, and the final pH (pH_f) was measured. By drawing plot of (pH_f - pH_i) *vs*. pH_i, the pHpzc was obtained.

Regeneration Study

After the equilibrium condition, the regeneration experiment was studied immediately. The PCA composite was saturated with 8 and 10 ppm MB and MO, then to remove the residual pigment particles, this solution was washed with water. The obtained PCA was dried and washed by methanol and ethanol. The adsorption tests was carried out with this composite and %removal was calculated using Eq. (2).

RESULTS AND DISCUSSION

Characterization of the Perlite-calcium Alginate-activated Carbon Composite

In this work, the perlite-calcium alginate-activated carbon composite was prepared and subsequently its performance as the adsorbent was investigated. Figure 1 illustrates the FTIR spectra of perlite, activated carbon, and perlite-calcium alginate-activated carbon.

In Fig. 2a, the FTIR spectrum of activated carbon can be observed. The peaks at 3100-3500 cm^{-1} belong to the O-H vibrations of the water. The C-O and C=O peaks are at the region of 1600-1650 cm^{-1} and the peaks between 1000-1200 cm^{-1} represent the C-O band. The distinctive peaks at 1400-1500 cm^{-1} indicate the presence of methylene groups [45].

The FTIR spectra of the impure and neat perlite are shown in Figs. 2b,c. In the FTIR spectra of the impure and neat perlite, five peaks are observed as the important absorption bands. The stretching and bending vibrations peaks at 3200-3500 cm^{-1} and 1633 cm^{-1} are assigned to the Si-OH and O-H (hydroxyl) groups and the adsorbed water. The Si-O-Si and Si-O-Al bands are indicated by the peaks at 1061-1063 cm^{-1} as stretching and 461-462 cm^{-1} as bending vibrations. In the neat perlite, weak infrared signals are observed due to its symmetry (Fig. 2c), and the removal of organic compound is indicated by absence of the peak at 1452 cm^{-1} in the impure perlite.

FTIR spectrum of the perlite-calcium alginate-activated carbon is depicted in Fig. 2d. The stretching of O-H groups, depicted at 3385 cm^{-1}, corresponds to hydroxyl vibrations. The appeared peaks at 1602 and 1423 cm^{-1} are attributed to alginate molecules, and the O-C-O stretching frequency was observed at 1026 cm^{-1} [46]. The Si-O stretching vibration is observed around 480-505 cm^{-1} that belong to perlite clay.

The X-ray diffraction (XRD) patterns of neat perlite and perlite-calcium alginate–activated carbon are shown in Fig. 3. The peaks at $2\theta = 27^{o}$ and $2\theta = 31^{o}$ confirm amorphous property of perlite. The formation of composite can be shown by the shift of peak at $2\theta = 27^{o}$ to $2\theta = 26^{o}$, due to change the symmetry of the perlite. Also, it can be confirmed loading of the activated carbon and alginate.

FE-SEM images of the neat perlite and perlite-calcium alginate-activated carbon are illustrated in Fig. 4. The layer of the neat perlite can be seen in Fig. 4a, and the bulges and beads of the calcium alginate at 3D network layer on the surface of PCA can be observed in Fig. 4b. SEM images could confirm the heterogeneous composite structure.

Figure 5 depicts the nitrogen adsorption-desorption isotherms for perlite-calcium alginate-activated carbon. The specific surface area and cumulative pore volume were obtained 158.16 $m^2\ g^{-1}$ and 0.060646 $cm^3\ g^{-1}$, respectively. The specific surface area of PCA was lower than that of activated carbon (158.16 $m^2\ g^{-1}$ contrast to 894 $m^2\ g^{-1}$), however, the preparation of PCA is an economical method requiring the lower amount of activated carbon, in contrast to using only activated carbon with the same %dye removal results. The type IV isotherm was investigated according to IUPAC classification, confirming the porous surface by its hysteresis loop [47]. The isotherm describes PCA as a mesoporous material, then it (4.6831 nm) can adsorb MB (1.382 nm). The microporous materials are not able to adsorb MB molecules.

Batch Adsorption Studies

In this work, the effects of different solution parameters including the pH, adsorbent doses, MB and MO quantities, contact time and temperature were studied for the adsorption on perlite-calcium alginate-activated carbon.

The amounts of the adsorbed MB and MO were calculated using Eq. (1), by the difference of the initial and residual amounts of dyes in solution divided by the mass of the adsorbent. The removal efficiency of the system, R_e (determined as the removal percentage of the pigments relative to the initial dose), was calculated using Eq. (2):

$$q_e = \frac{(C_i - C_e)\,V}{m} \tag{1}$$

$$R_e = \frac{(C_i - C_e)}{C_i} \times 100 \tag{2}$$

where q_e (mg g^{-1}) is the amount of MB and MO adsorbed per unit mass of the perlite-calcium alginate-activated carbon. The C_i and C_e are the initial and equilibrium (or at any time) doses (mg l^{-1}), respectively. v is the volume of the solution in litre, and m is the mass (g) of the perlite-calcium alginate-activated carbon.

Effect of pH

The pH of the solution plays an important role in the process of adsorption, since it can affect the ionization of the solution and the adsorption on the adsorbent surface [48]. The effect of pH on adsorption of MB and MO is illustrated in Fig. 6a. The yield of the adsorption was investigated within the pH range of 2-12. The highest yields for the adsorption of MB and MO were obtained at pHs of

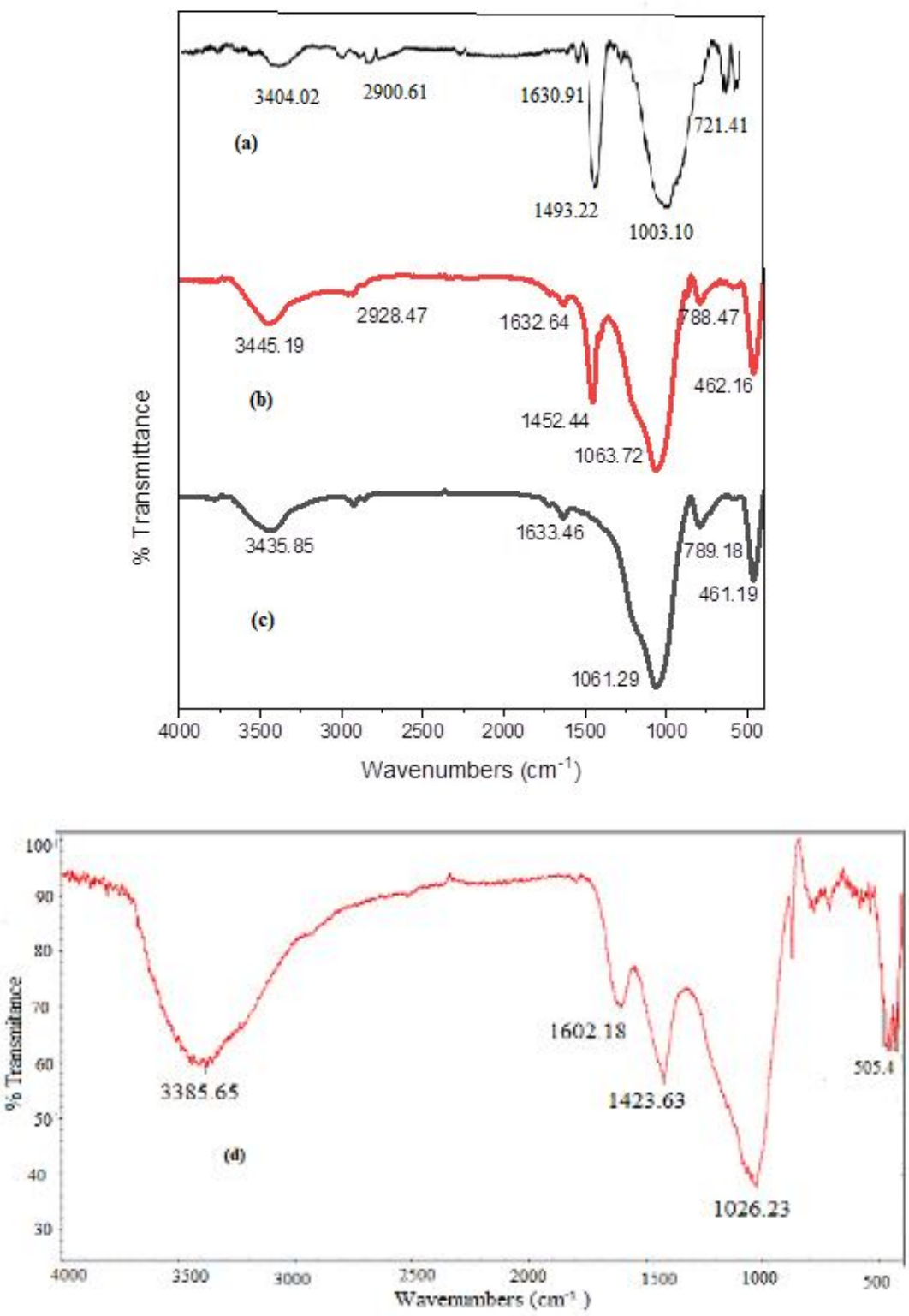

Fig. 2. FTIR spectra of (a) perlite, (b) neat perlite and (c) perlite-calcium alginate-activated carbon.

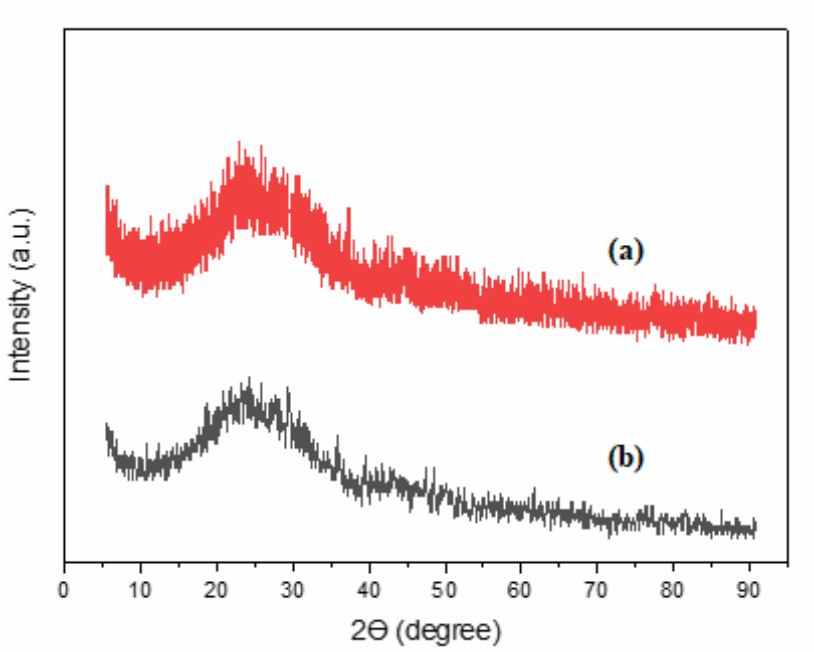

Fig. 3. XRD patterns of (a) the neat perlite and (b) perlite-calcium alginate-activated carbon.

8 and 3, respectively. The pH of 6.8 was found as pH_{pzc} for the perlite-calcium alginate-activated carbon. It was confirmed that pH < 6.8 results in positive surface charge of the PCA; therefore, this range was suitable for the adsorption of anionic dyes such as MO. When the pH is higher than pH_{pzc}, the MB can be adsorbed on the negative charge of the perlite-calcium alginate-activated carbon's surafce.

Effect of Adsorbent Dosage

The effect of perlite-calcium alginate-activated carbon dosage is illustrated in Fig. 6b (the range of 0.006-0.15 g of adsorbent). Results of the experiments indicated that the increase in perlite-calcium alginate–activated carbon doses leads to a high surface area and the dye removal is increased. The best results were achieved at 0.01 and 0.008 g of adsorbent for MB and MO, due to increase of adsorbent surface. By increasing the PCA dose more than these values, the adsorption efficiency did not change significantly [49].

Effect of MB and MO Doses

Initial dye dose has important role to transfer the mass between dyes and adsorbent. The effects of MB and MO doses (2-22 ppm) were investigated for the adsorption on PCA (Fig. 7a). The optimum MB and MO doses were obtained at 10 and 8 ppm where the driving force resulted in the interaction between PCA respectively. At lower doses, there were empty active sites on the adsorbent surface. When the adsorbent active sites were saturated, the repulsion between the adsorbent surface and dyes was increased.

Effect of Contact Time

The effect of contact time on the biosorption process is plotted in Fig. 7b. The results showed that by increasing the initial time from 5 to 120 min, the adsorption efficiency of MB increases for these adsorbents. However, at times more than 120 minutes, no significant change was observed in the removal of MB using the aforementioned adsorbents.

Experiments were carried out to discover the effect of the contact time for the removal of MB and MO from aqueous solutions, by increasing the initial time from 15 to 360 min. The maximum efficiencies were investigated at 60 min (Fig. 7b), at more than 60 min, the adsorption efficiency of dyes did not change significantly. At

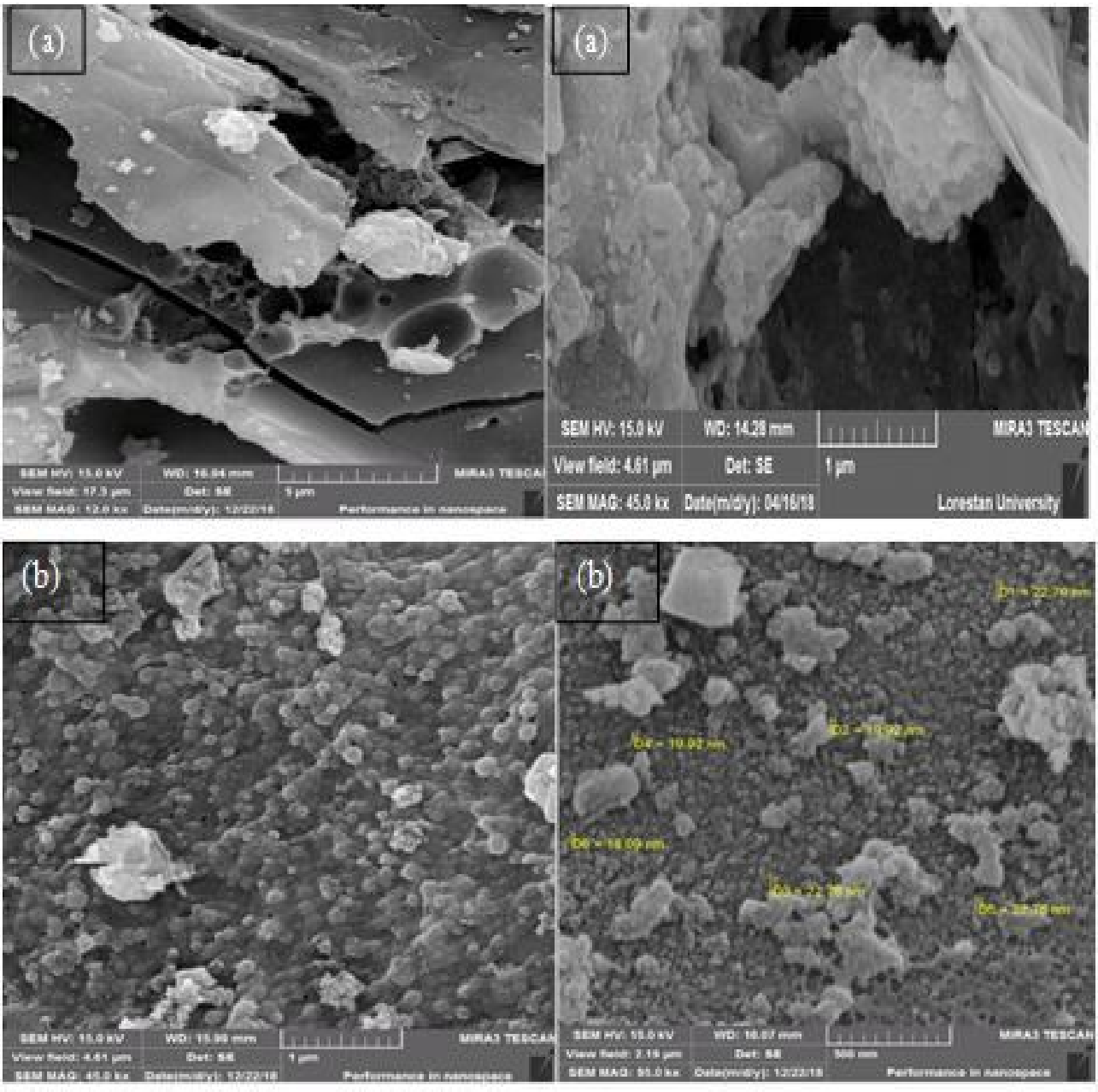

Fig. 4. SEM images of (a) the neat perlite and (b) perlite-calcium alginate-activated carbon.

time <60 min, the adsorption efficiency was increased because of a sufficient and unsaturated active surface.

Effect of Temperature

The equilibrium temperature for the removal of dyes is illustrated in Fig. 8. The efficiencies regarding the temperatures were obtained for both pigments. The optimum temperature range was determined as 15-20 °C; when the temperature was elevated, the removal percentage was diminished. With increasing temperature, the

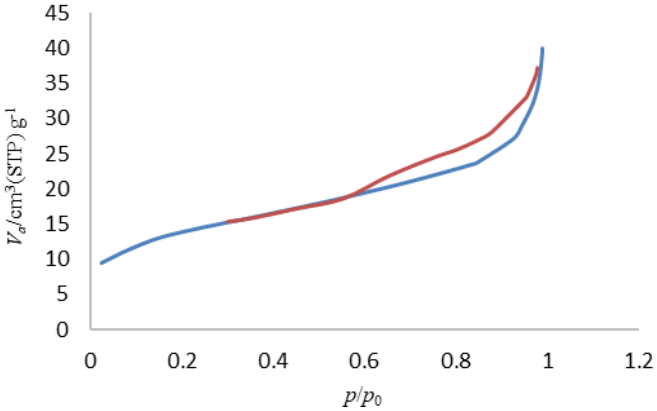

Fig. 5. The N_2 adsorption-desorption isotherm of perlite-calcium alginate-activated carbon.

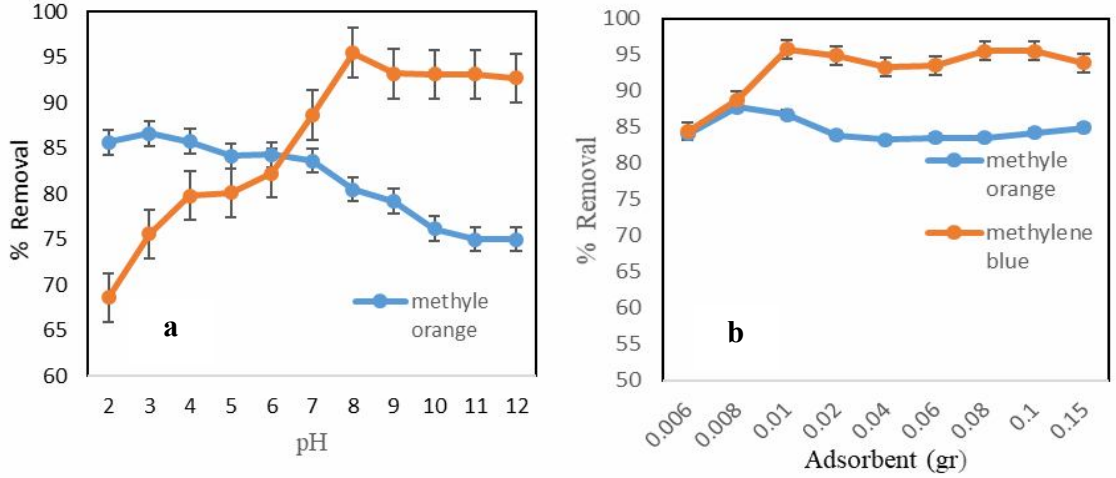

Fig. 6. The effects of (a) pH and (b) adsorbent doses for MB and MO adsorption on PCA.

adsorption efficiency was decreased due to an increase in the diffusion rate of the pigment out of the boundary layers of PCA, therefore, the low temperature was approved for adsorption of MB and MO on PCA. Finally, the system was found to be exothermic.

Adsorption Kinetics

The pseudo-first order and pseudo-second order rate equations were used to obtain the kinetics models [50]. The pseudo-first order kinetics rate Eq. (3) was expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

where q_e and q_t (mg g^{-1}) are the amounts of MB and MO, respectively, and K_1 is the rate constant (1/min) (slope of the linear plot of ln (q_e - q_t) *vs.* t).

In addition, the pseudo-second order reaction rate equation was applied to assess the kinetics of the MB and MO adsorption on perlite-calcium alginate-activated carbon:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

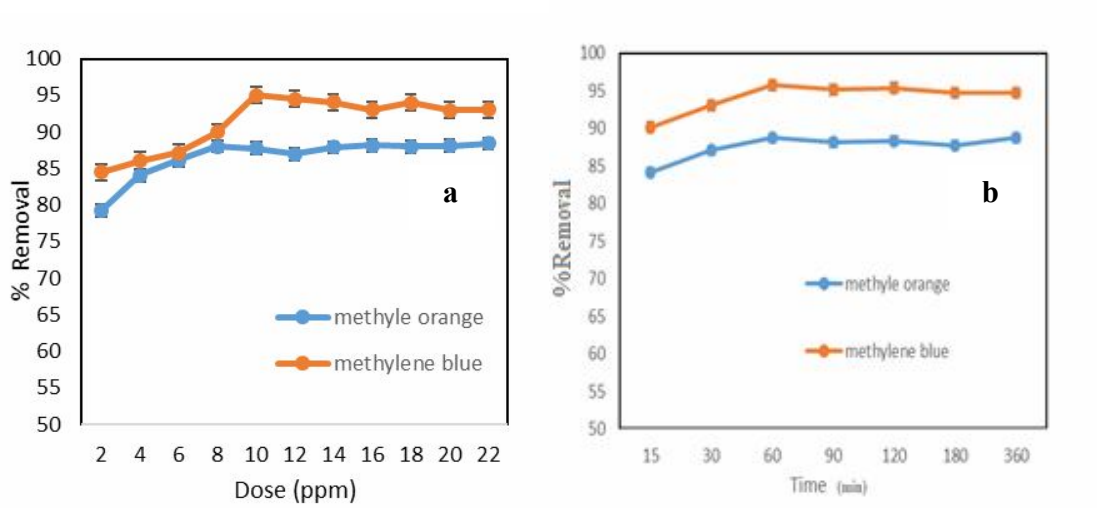

Fig. 7. The effect of (a) MB and MO doses and (b) contact time of the MB and MO adsorption on PCA.

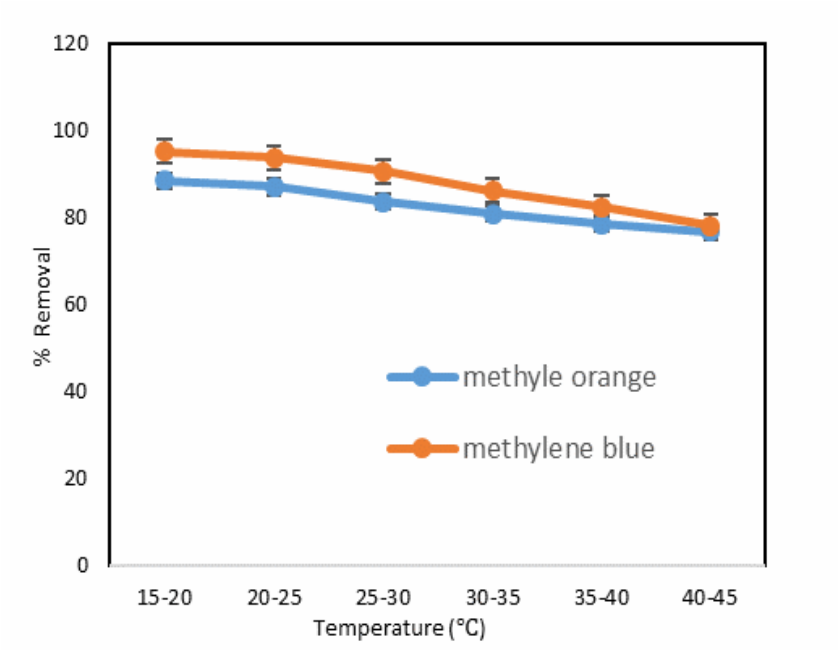

Fig. 8. The effect of temperature on MB and MO adsorption by PCA.

where q_e and q_t are the amounts of MB and MO adsorbed on the perlite-calcium alginate-activated carbon (mg g^{-1}) and K_2 is the rate constant of the pseudo-second order adsorption (g mg^{-1} min^{-1}).

The kinetics plots of t/q_t *vs.* t were constructed for different initial doses (Figs. (9)-(10)).

The slope and intercept values were corresponded to pseudo-second order equation for MB and MO. It was clear that MB and MO adsorption on PCA followed the pseudo-second order kinetic model, because the R^2 value from this kinetic model was found to be closer to 1 compared to that of the pseudo-first-order kinetic model. Also, the value of q_e

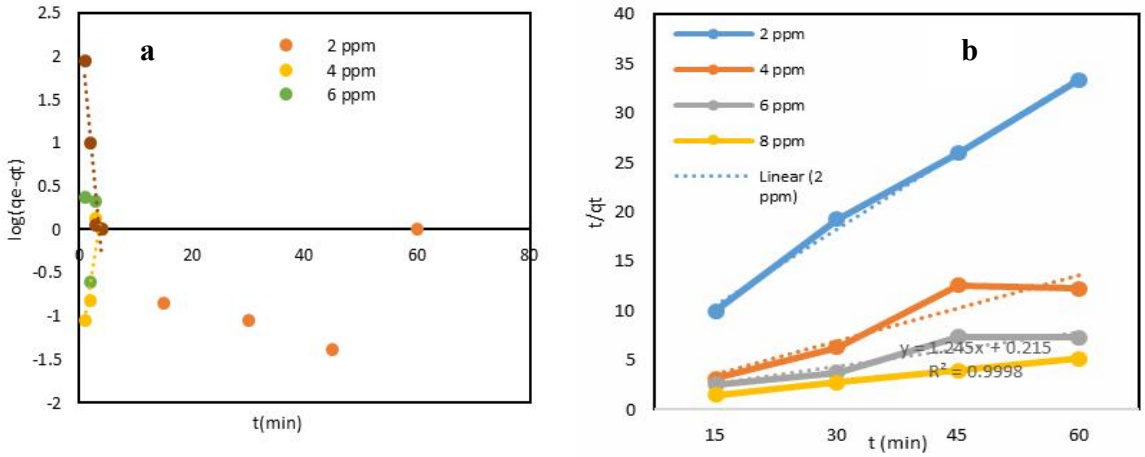

Fig. 9. (a) pseudo-first-order and (b) pseudo-second-order kinetic graphs for MO adsorption on PCA.

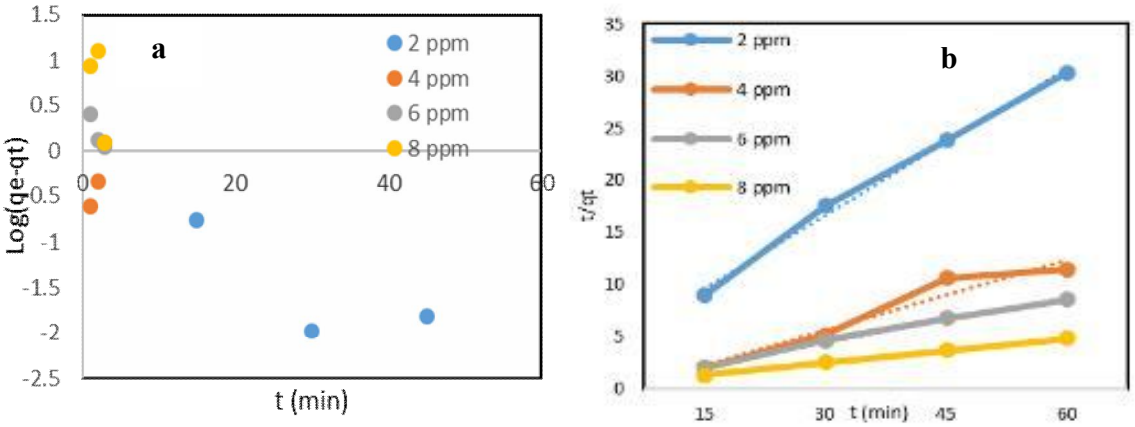

Fig. 10. (a) pseudo-first-order and (b) pseudo-second-order kinetic graphs for MB adsorption on PCA.

from pseudo-second order kinetic model was near to the obtained experimental q_e. The adsorption of MB on PCA was a chemical adsorption, since increasing the MB dose resulted in a decrease in k_2 values (Table 1).

Adsorption Isotherm

The adsorption isotherms help to design the model of the adsorption systems, and to determine the corresponding mechanisms. In this research, the Freundlich and Langmuir isotherms were selected to study the adsorption process [51,52].

The homogeneous sites and monolayer adsorption take place in the Langmuir adsorption. The linear forms of the Langmuir and Freundlich Eqs. ((5) and (6)) can be written as below [52,53]:

$$\log q_e = \frac{1}{n}\log C_e + \log K_f \quad (5)$$

$$\frac{C_e}{q_m} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (6)$$

q_e: the adsorbent amount (mg g^{-1}) of the MB and MO

C_e: the equilibrium dose of the MB and MO at solution (mg l^{-1})

K_f and n: the model constants showing the relationship

Table 1. Kinetic Parameters for MB Adsorption on PCA

C_0 (mg l^{-1})	Pseudo-first-order			Pseudo-second-order			q_e,exp (mg g^{-1})
	K_1 (min^{-1})	q_e,cal (mg g^{-1})	R^2	K_2 (g mg^{-1} min^{-1})	q_e,cal (mg g^{-1})	R^2	
2	0.46	240	0.63	2.67	440	0.9942	432
4	0.42	275	0.62	1.82	375	0.9384	379
6	0.17	169	0.88	1.47	460	0.9930	451
8	0.35	266	0.97	1.07	860	0.9999	856

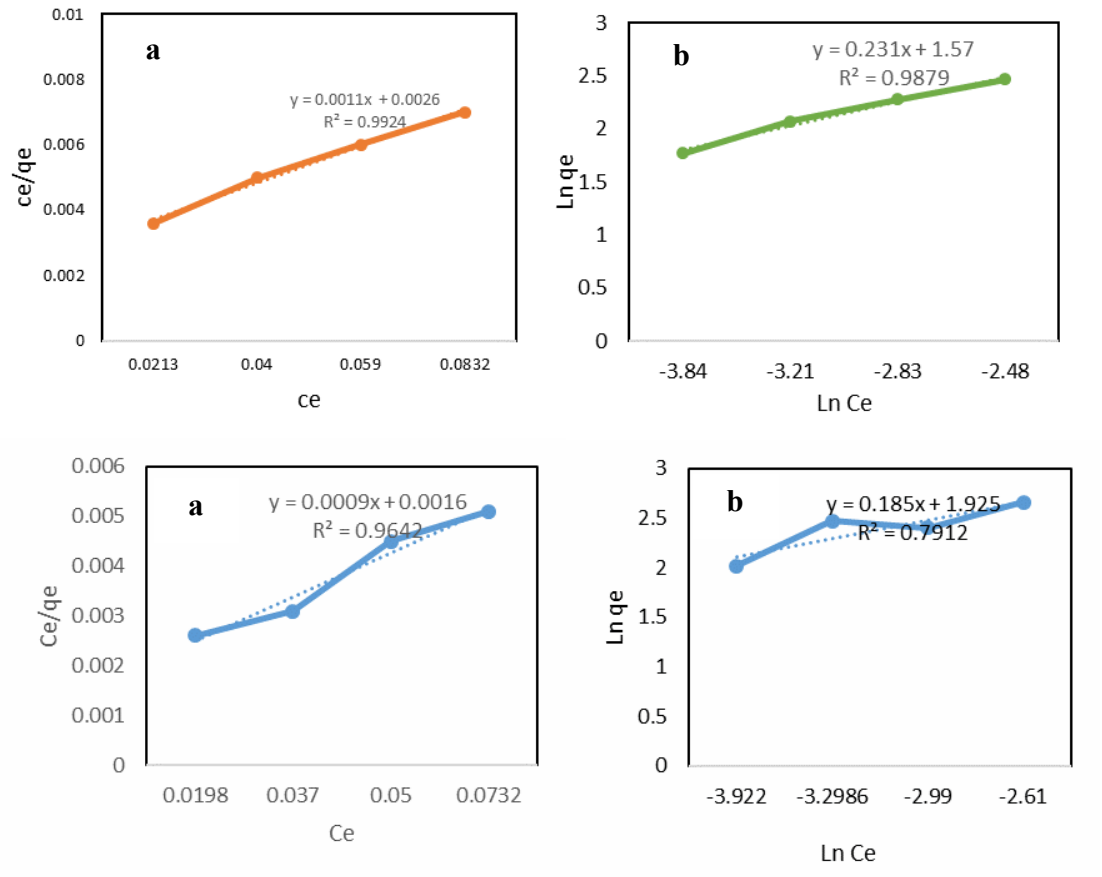

Fig. 11. Langmuir and Freundlich isotherm plots for adsorption of (a) MO and (b) MB on PCA.

Table 2. Information of the MB and MO Adsorption Isotherm Models on PCA

Organic pollutants	Freundlich			Langmuir		
	k_f (mg g^{-1}) (mg l^{-1})^2	n	R^2	Q_{max} (mg g^{-1})	b (l mg^{-1})	R^2
MB	6.85	5.40	0.79	1111	1.35	0.9981
MO	4.80	4.32	0.98	909	0.42	0.99

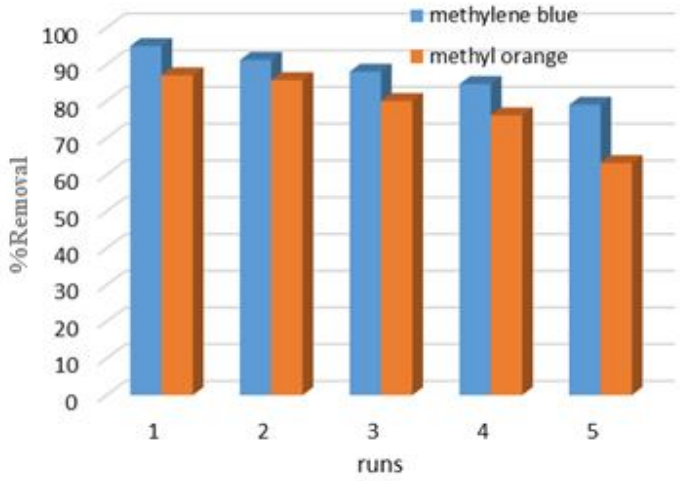

Fig. 22. The effect of runs on MB and MO adsorption on PCA.

between adsorption capacity and adsorption intensity
q_m: monolayer adsorption capacity (mg g^{-1})
b: the constant related to the free energy of the adsorption (l mg^{-1}).

The values of Freundlich and Langmuir constants determined are shown in Table 2. The process of MB and MO adsorption followed the Langmuir model (Fig. 11). In the present study, the MB and MO adsorption processes were far more fitted to Langmuir model (R^2 = 0.998 and 0.99) compared to Freundlich model (R^2 = 0.79 and 0.98). The q_m was obtained by 1111 and 909 mg g^{-1} for MB and MO, respectively, indicated the high capacity of PCA for adsorption of the studied dyes. In Frendlich isotherm, the value of n > 1 shows desirable adsorption, which was obtained 5.40 and 4.32 for MB and MO, respectively.

Regeneration Studies

The performance of PCA can be evaluated by regeneration study of the adsorbents. In the current work, the reusability of PCA was found even after five cycles (Fig. 12). Also, the sorption-desorption tests indicated the proper economic and environmental impacts of the adsorbent.

Moreover, the yield of the removal of pigments by PCA was compared to those of the perlite, activated carbon, and the alginate individuality, in this work and in the literature (Table 3). Activated carbon was used extensively for dyes removal, due to high specific surface area. An important

limitation of activated carbon is the costs of preparation and system sustainability by using a raw material that is not perpetual. In this study, we have used lower amount of activated carbon compared to when only activated carbon was used [54,55]. The efficiency of perlite-calcium alginate-activated carbon was highlighted, suggesting the development of an innovative and high yield adsorbent. The as-prepared adsorbent proved to adsorb organic materials with good reusability properties.

CONCLUSIONS

In this work, a novel green adsorbent was prepared and characterized for the first time. The scanning electron microscopy, Brunauer-Emmett-Teller, X-ray diffraction, and Fourier-transform infrared spectroscopy techniques were applied to obtain the properties of the perlite-calcium alginate-activated carbon (PCA) composite. The removal of methylene blue (MB) and methyl orange (MO) was studied in aqueous solutions. The optimization of various solution parameters including pH values, amounts of the PCA, MB and MO doses, contact time and temperature were evaluated. The Langmuir equation was suitable for equilibrium experiments and the pseudo-second-order kinetic model could successfully describe the dynamic experiments. The adsorption of organic pollutants was chemical, and exothermic. The as-prepared adsorbent exhibited unique properties such as highly enhanced capacity, simple strategy for preparation, and easy regeneration. It also displayed a good performance compared to individual structures. Overall, the current study demonstrated a new, highly efficient, economical and reusable adsorbent for the removal of toxic pigments.

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