Adsorption of methylene blue dye from aqueous solution by a novel PVA/CMC/halloysite nanoclay bio composite: Characterization, kinetics, isotherm and antibacterial properties

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Abstract

Here the fabrication of a novel PVA/CMC/halloysite nanoclay membrane for the effective adsorption of cationic dye (methylene blue, MB) from aqueous environment is reported. The membranes were analyzed through scanning electron microscopy (SEM), optical microscopy (OM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), contact angle and universal testing machine (UTM) analysis. The adsorption behavior of the membrane in terms of nanoclay loading, contact time, initial concentration of MB, pH and temperature were also discussed. The membrane exhibits excellent removal efficiency (99.5%) for MB in the optimal conditions such as nanoclay dose = 6 wt%, initial dye concentration = 10 ppm, contact time = 240 min, pH = 10 and temperature = 30 °C. Three isotherm models (Freundlich, Langmuir and Temkin) were employed to analyze the dye adsorption data. The results revealed that the adsorption process could be described well with both Freundlich and Langmuir isotherm model. The kinetics of MB adsorption onto membrane follows pseudo-second-order model while thermodynamic parameter indicate that adsorption is feasible and endothermic in nature. The antibacterial studies revealed that the PVA/CMC/halloysite nanoclay membrane possess notable antibacterial property. Finally, the desorption studies showed that the membrane have good reusability even after four recycles.

Keywords Halloysite nano clay · Bio-composite · Adsorption mechanism · Methylene blue · Isotherm models · Kinetics · Thermodynamics

Introduction

Water pollution is a global issue which is rising in an alarming rate. It has a serious impact on the climate, food chain and to our ecosystem. Hence researchers all over the globe have focused their attention to develop an efficient treatment method to tackle this issue [4, 9, 10, 59, 68, 92]. Adsorption process is one of the best choices for the removal of toxic contaminants from water as it possesses many

benefits over other treatment method such as flocculation, ion exchange, electrochemical treatment, photocatalytic degradation, biodegradation etc. [12, 14, 15, 22, 23, 46, 81, 82]. The adsorbent which is cheap, non-toxic and environmental-friendly is preferred over toxic and synthetic adsorbent. Researchers are in search of low-cost and ecofriendly adsorbent for the removal of contaminants from water [7, 8, 30, 36, 70]. Clay is a fine particle (less than 2 µm size) which is mainly composed of silica, alumina and water. This cheap and ecofriendly material is abundantly found on the earth crust and possesses some attractive features such as high porosity, high ion-exchange ability, high specific surface area, good thermal stability and adsorption power [2, 18, 27, 29, 54, 76, 77, 87]. Over the year's researchers have explored the application of clay as adsorbent, air purifier, catalyst etc. [50, 61, 84, 94]. For the last several decades, both natural and modified clay has been used to remove the toxic containments from water [35, 38, 47, 63]. Clay have been successfully employed to develop several nanocomposites whose adsorption capacity matches well with

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conventional adsorbent. Previous studies show that clay-based composites could act as a promising candidate for dye removal studies [58, 85].

Methylene blue (MB) ($C_{16}H_{18}ClN_3S$) is a cationic dye which is widely used as colorant in textile, wood and paint industries. It is also used in biochemistry laboratory to stain specimens such as bacterial/animal cells and tissues [3, 20, 39, 48, 65]. MB when administered in therapeutic dosage is effective for the treatment of methemoglobinemia, cyanide poisoning and urinary tract infection [40, 51, 57]. In spite of its application in several industries, MB is toxic in nature and will adversely affects both humans and animals. The major health issues in humans are headache, vomiting, diarrhea, sore eyes, cyanosis, Heinz body formation, delirium and tissue necrosis [34, 45, 93]. MB mainly enter into the water bodies through chemical industries, and it remain as persistent pollutant in water. It is important to point out that the dark blue color of MB shields the sunlight from entering the water bodies and thereby decrease the dissolved oxygen content of water. Hence it have an adverse impact on the aquatic flora and fauna [1, 98]. Researchers have fabricated several adsorbent systems for the removal of MB from waste water [21, 62, 80]. Somsesta et al. [83] fabricated carbon/cellulose composite film by solution casting method and demonstrated its dye adsorption property. The result showed that membrane loaded with high percentage of carbon exhibits good adsorption capacity (103.66 mg/g) and could act as an effective adsorbent for MB. Polyvinyl alcohol composites incorporated with nanomaterials such as TiO_2 and zeolite was reported to have an impressive MB removal efficiency. The negative charge present on the surface of the composites leads to greater affinity between cationic MB and the composite [13, 43, 74]. A similar type of adsorbent system was fabricated by Bayat et al. [16] from zeolite, nickel ferrite and sodium alginate.

Carboxy methylcellulose (CMC) is an anionic polymer which is eco-friendly and abundantly available. Due to the presence of large number of hydroxyl group, it has high propensity to attract positively charged molecules [72]. Therefore, it has been employed for the removal cationic dye [19, 73]. For instance, Begum et al. [55] investigated the MB adsorption performance of CMC. The authors reported that the dye adsorption could be enhanced by increasing the degree of substitution. This is attributed to the presence of large number of hydroxyl group on the system. Ting and co-workers [86] developed a bio-adsorbent from CMC and tannin for MB removal. The greater improvement in the adsorption performance is ascribed to the combined presence of negatively charged functional groups such as hydroxyl and carboxyl group in the system. Liu and co-worker [53] prepared CMC/k-carrageenan/montmorillonite (MMT) composite beads for methylene blue removal under different adsorption condition. The composite loaded with 0.4% of MMT displayed 92% removal within short period of time.

To best of our knowledge, there is no report available on the usage of halloysite nanoclay-CMC membrane for MB removal from aqueous environment. This prompted us to fabricate a novel halloysite nanoclay-based membrane for the removal of cationic dye, MB from water. The membrane was prepared by solvent casting technique by incorporating carboxymethyl cellulose (CMC) and halloysite into polyvinyl alcohol (PVA), which is a cheap and ecofriendly polymer. The morphology and the chemical properties of the membranes were discussed briefly. The role of different operational parameters such as nanoclay loading, initial dye concentration, contact time, pH and temperature on the adsorption behavior of PVA/CMC/halloysite nanoclay was investigated. The adsorption isotherm and kinetics of MB adsorption on the membrane is also highlighted. We also performed thermodynamics studies to understand the nature of adsorption process. The antibacterial activity and recyclability of the membrane is also described briefly in this article.

Materials and methods

Materials

Polyvinyl alcohol (PVA, C_2H_4O , Mw = 130,000: hydrolysis degree: 99%) was obtained from Ajax Finechem Pvt. Ltd. (Thailand). The crosslinking agent glutaraldehyde ($C_5H_8O_2$; GA) and methylene blue (MB, $C_{16}H_{18}ClN_3S$) was purchased from Loba Chemie Products Limited. (Thailand). Carboxymethyl cellulose (CMC, $(C_6H_7O_2(OH)_x(OCH_2COONa)_y)_n$) was provided by Chemipan (Thailand). Halloysite nanoclay was purchased from Sigma Aldrich (Sigma Aldrich, Singapore). All materials were used without further purification.

Fabrication of the PVA/CMC/halloysite nanoclay membrane

At first, 8 wt% of PVA was prepared by dissolving required amount of PVA in distilled water with continuous stirring at 90 °C for 5 h. To the cooled PVA solution, 3 wt% of CMC solution were added dropwise under constant stirring. Afterwards, different percentage (2, 4 and 6 wt%) of halloysite nanoclay was mixed with blended PVA/CMC solution. To attain homogeneity, the mixture was kept under stirring for another 12 h at room temperature. The cross-linking of the membrane was established by using 2.5% of glutaraldehyde (GA) and 3% of HCl. Finally, the viscous solution was poured into a petri dish and dried at room temperature for 6 days. After drying, the membrane was peeled out from the petri dish and used for further characterization. The membrane loaded with 0, 2, 4 and 6 wt% of halloysite nanoclay was designated as PCC-0, PCC-1, PCC-2 and PCC-3 respectively. The membrane

thickness was measured by screw gauge at different positions and the thickness was found to be $25 \pm 2 \mu\text{m}$ [64].

Dye adsorption studies

The dye adsorption studies were conducted by agitating 0.06 g of membrane with 50 mL of methylene blue dye solution at 200 rpm in room temperature. After a certain interval, the dye solution was separated by centrifugation at 10000 rpm for 15 min. The absorbance of the dye solution was analysed spectrophotometrically (Specord (UV-210)) at a characteristic wavelength of 665 nm. The experimental parameters such as nanoclay dosage, contact time, initial concentration of MB, pH and temperature on the adsorption capacity of membrane was investigated. The amount of dye adsorbed per unit mass of adsorbent (q_e) and percentage dye removal efficiency (R%) were calculated by using the following equations:

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

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

where C_0 and C_e (mg/L) are the concentrations of MB solution before and after adsorption, respectively; V (L) is the volume of the aqueous MB solution and W is the weight of the membrane (g).

Desorption and reuse experiments

For reusability test, the saturated membrane was dipped in acid solution (0.1 N HCl) solution for 3 h. Later the membrane was taken out, washed, dried in air and was used for next recycle test [25].

Characterisation

X-ray diffraction (XRD) studies

The overall crystallinity of the membrane was tested by Rigaku miniflex 600 benchtop using Cu-K α as radiation source. All samples were scanned over 2θ range of $5\text{--}50^\circ$ with a scan speed of $2^\circ/\text{min}$.

Fourier-transform infrared

FTIR spectroscopy were used to observe the chemical composition of the membrane. PVC/CMC/ halloysite nanoclay membrane with different content of clay were measured with Jasco 4700 FT-IR spectrometer equipped with ATR. The sample was scanned in the frequency range of $450\text{--}4000 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} .

Scanning electron microscopy

The distribution of halloysite nanoclay particles in the PVA/CMC matrix and the surface morphology were evaluated by using scanning electron microscope (FEI Quanta 450) and optical microscope (Olympus BX43 series instrument).

Thermogravimetric analysis

Thermal decomposition studies of the dried membrane in the temperature range of $50\text{--}750^\circ\text{C}$ were examined using Mettler Toledo TGA/DSC 3 + HT/1600 with a heating rate of $10^\circ\text{C}/\text{min}$ under N_2 atmosphere.

Mechanical properties

Mechanical properties of the membrane were studied by using UTM (Universal testing machine, QC-506 M1–204). Test specimen were cut into rectangular shape with $50 \text{ mm} \times 15 \text{ mm}$ dimensions and the tests were performed with cross-head speed of $10 \text{ mm}/\text{min}$ with 10 kN load.

Water contact angle measurement

The wettability of the membranes was assessed by noting water contact angle, measured using a Drop Meter SCA data physics contact angle system equipped with a camera. $2 \mu\text{L}$ of distilled water was dropped on the membrane surface using a micro syringe and the camera captured the water droplet. All measurement was carried at least five times at different membrane surface and average of the results were taken.

Water absorption

The degree of swelling of membranes were measured by immersing dried membrane with $2 \times 2 \text{ cm}$ dimension in 10 mL distilled water for 24 h. After a predetermined interval, the swollen membranes were take-out and the excess water was removed with tissue paper and weighed until a constant weight is observed. The degree of swelling (DS) is calculated using the following equation:

$$\text{Degree of swelling (\%)} = \frac{W_1 - W_0}{W_0} \times 100$$

where W_1 and W_0 are weight of dried and swollen membrane respectively.

Antibacterial activity test

The antibacterial activity of the membranes against *Staphylococcus aureus* and *Escherichia coli* as gram-positive and gram-negative bacteria was evaluated by disc diffusion

method. 100 μL of bacterial culture was swabbed uniformly on the surface of agar covered plates and the plates were kept for incubation at 37 $^{\circ}\text{C}$ for 24 h. The membranes were then punched to make disks with 5 mm thickness and placed on agar plate and incubated at 37 $^{\circ}\text{C}$ for 24 h. The inhibition zone that formed around the membrane was noted.

Result and discussion

Characterization of PVA/CMC/ halloysite nanoclay membrane

The structural feature and the chemical composition of the membrane were evaluated by XRD. The XRD pattern of membrane with different percentage of halloysite nanoclay (2 wt%, 4 wt% and 6 wt%) is shown in Fig. 1a. The neat PVA/CMC membrane displayed a sharp reflection at $2\theta = 20^{\circ}$, corresponding to the (101) lattice planes of PVA and semi crystalline nature of CMC [78, 100]. An additional peak appeared at $2\theta = 12.1^{\circ}$ for nanoclay loaded membrane corresponds to the reflection from (001) plane of halloysite nanoclay [32]. Furthermore, it can be observed from Fig. 1a that the intensity of peak centered at $2\theta = 20^{\circ}$ increases with nanoclay loading and is attributed to characteristic (020) plane of clay [99]. The XRD data thus suggest that nanoclay is successfully incorporated in PVA/CMC membrane. The FTIR spectra of the neat PVA/CMC and PVA/CMC membrane loaded with different percentage of halloysite nanoclay are shown in Fig. 1b. The strong peak observed at 3286, 2942 and 1433 cm^{-1} are ascribed to the O–H stretching, C–H stretching and C–H bending of PVA and CMC respectively [17, 95]. The peak appeared at 1069 cm^{-1} corresponds to the C–O stretching of PVA, CMC and Si–O stretching of clay [24]. The appearance of new peak at 525 cm^{-1} is attributed the Al–O–Si deformation bond of clay. Thus, FTIR findings are in agreement with those

deduced from XRD analysis. The surface morphological features of the membranes are assessed by SEM analysis (Fig. 2a). It can be noted that when compared to neat PVA/CMC membrane, nanoclay loaded membranes displayed a rough surface. This could be due to the dispersion of nanoclay particle on the polymer matrix. Moreover, the particle density on the surface of membrane increases with clay loading and membrane loaded with 6 wt% of nanoclay (PCC-3) displayed high roughness. A similar trend in surface morphology is reflected in the optical micrographic images (Fig. 2b). The hydrophilicity of the membrane was assessed by water contact angle measurement. The neat PVA/CMC membrane give high contact angle value (78 $^{\circ}$) indicating the hydrophilic nature of the membrane (Fig. 3a). Upon addition of halloysite nanoclay, the contact angle value decreases and the contact angle value of 2, 4 and 6 wt% nanoclay loaded membrane is found to be 71.9 $^{\circ}$, 65.7 $^{\circ}$ and 54.3 $^{\circ}$ respectively. The results thus indicate that the PVA/CMC/halloysite nanoclay membrane possess good hydrophilic character, ascribed to the porous nature of clay [66, 91]. Swelling characteristics of the membrane plays an important role in adsorption studies. Swelling behavior of PVA/CMC membrane as a function of nano clay loading is shown in Fig. 3b. As can be seen from Fig. 3b that on increasing the nano clay content from 2 to 6 wt.%, the degree of swelling increase from 74 to 113%. Thus, incorporation of halloysite nanoclay facilitates the movement of water molecules to the membrane.

The thermal property of the membranes was characterized through thermogravimetric analysis (Fig. 3c). For PVA/CMC/halloysite nanoclay membrane, three stages of thermal degradation were observed. The initial degradation observed at 100–150 $^{\circ}\text{C}$ is due to loss of adsorbed water molecules from the membrane while the major degradation observed in the range of 290–350 $^{\circ}\text{C}$ corresponds to decomposition of CMC and PVA polymer. The final degradation in the range of 410–600 $^{\circ}\text{C}$ is attributed to the decomposition of halloysite nanoclay. Table 1

Fig. 1 X-ray diffraction and FTIR spectra of plain PVA/CMC and PVA/CMC prepared with different loadings of halloysite nanoclay

Fig. 2 **a** SEM and **b** optical microscopic images micrographs of PVA/CMC loaded with different percentage of halloysite nanoclay

shows the weight loss of the membrane at different temperature. It can be noted that on increasing the clay content from 2 wt% to 6 wt%, the total weight loss of the membrane decreases from 82.33 to 64.26%. Hence, membrane loaded with high nanoclay content has high thermally stability, which is desirable for adsorption studies [67, 90]. We further extend our study by investigating the tensile strength and elongation at break of the membrane as a function of nano clay (Fig. 3d & e). It is evident from

Fig. 3d the incorporation of nanoclay into PVA/CMC membrane will leads to an improvement in the tensile strength of the membrane. According to previous report [33, 79] the good bonding between clay and the polymer matrix will enable effective load transfer between clay and the polymer matrix. Therefore, incorporation of nanoparticle will improve the tensile strength of the composite. However, elongation at break decrease with halloysite nanoclay content.

Fig. 3 a Water contact angles b percentage degree of swelling c TGA d tensile strength and e % of elongation of halloysite nanoclay loaded PVA/CMC membrane

Adsorption studies

The MB dye uptake ability of the membrane was studied as a function of nanoclay dosage, contact time, initial dye concentration, pH and temperature. Initially, the effect of nanoclay content on adsorption capacity (q_e) of the membrane was

studied (Fig. 4a). It can be seen that with increase in nanoclay content, the adsorption capacity of membrane increases and a maximum adsorption capacity (8.29 mg/g) was noted for membrane loaded with 6 wt% of clay (PCC-3). The result thus shows that nanoclay content plays a crucial role in controlling the adsorption capacity (q_e) of the membrane. Scheme 1

Table 1 Weight loss at different temperature on PVA/CMC/halloysite nanoclay membranes

Samples	Weight loss %			Total weight loss %
	100–150	290–350	400–600	
PCC-0	11.42	42.85	36.65	90.92
PCC-1	25.17	23.84	33.32	82.33
PCC-2	6.97	33.37	29.22	69.56
PCC-3	6.03	34.88	23.35	64.26

depicts the schematic representation of nanoclay content on the adsorption process. Our finding correlated well with the previous reports [41, 69]. Here the authors claimed that adsorbent dosage can increase the surface area and vacant adsorption site on the membrane. In addition to this, adsorbent dosage can also influence the surface charge of membrane. In the light of the above reports, we can say that membrane loaded with high amount of nanoclay has greater chance to adsorb MB molecules, as it possesses fairly good surface area and large number of vacant adsorption sites. Moreover, owing to its negative charge, clay loaded membrane have greater tendency to attract cationic MB molecule (electrostatic attraction). The effects of contact time on the MB removal efficiency (R%) have been shown in Fig. 4b. As in Fig. 4b, in the initial contact time, adsorption capacity rises rapidly; ascribed to the availability of large number of vacant adsorption site. Thereafter, the adsorption capacity slows down due to the exhaustion of adsorption site. Eventually, after 4 h, an equilibrium is attained as the entire vacant site gets occupied by dye molecules. A similar trend was reported by El Shamy for polyvinyl alcohol (PVA/CZnO₂) nanocomposite system. The composite exhibits maximum MB adsorption for 30 min contact time [31]. Figure 5 shows the UV visible spectra of MB at different contact time interval in 50 mL of the membrane. To investigate the role of initial dye concentration on the adsorption capacity and removal efficiency of the membrane, we have varied the initial MB concentration from 10 to 110 ppm (Fig. 4c). As shown in Fig. 4c, with increase in initial MB concentration the adsorption capacity increases from 8.29 to 80 mg/g but the removal efficiency decreases from 99.5% to 87.2%. With increase in initial concentration, the ratio of MB molecule to the adsorbent increases. High initial dye concentration also provides necessary driving force for the mass transfer between solid to liquid phase. Hence, with increase in initial dye concentration, the interaction between MB and membrane increases which is reflected in its high q_e value. Similar observation was reported by Jawad et al. for the dye adsorption behavior of mesoporous Irani red kaolin clay [44]. In their work, with increase in initial dye concentration (10 to 120 mg/L) the adsorption capacity rises (2.2 to 1016 mg/g). The decreases in removal percentage with increase in initial

dye concentration is attributed to the fact that for a fixed weight of membrane, the free binding site available on the surface of the membrane get reduced. This result well correlated with reports of Somsesta et al. [83]. The temperature effect was evaluated by performing the adsorption studies at different temperature ranging from 30 to 70 °C and the data obtained is graphically represented in Fig. 4d. It can be noticed that on increasing the temperature from 30 to 70 °C, the adsorption capacity decreases from 8.29 to 7.6 mg/g. The decrease in adsorption capacity could be due to the exothermic nature of adsorption. Furthermore, elevated temperature also weakens the electrostatic interaction between MB and the membrane [52, 88, 89].

Solution pH is found to influence the charge density of adsorbent and therefore could alter the adsorbate-adsorbent interaction. This prompted us to investigate the effect of solution pH on the MB adsorption of PVA/CMC/halloysite nanoclay membrane by keeping other parameter constant (adsorbent dosage = 6 wt%, initial CR concentration = 10 ppm, contact time = 240 min and temperature = 30 °C). It is evident from Fig. 4e that the MB uptake ability of the membrane increases with pH. A maximum adsorption capacity (8.29 mg/g) was achieved when pH reaches 10. This trend of absorption capacity with pH is previously been reported by several researchers [25, 28] and explained on the basis of variation of surface charge density of adsorbent. At acidic pH, due to the presence of large number of H⁺ ion, the surface of adsorbent will become positive. This create an unfavorable repulsion between cationic MB and the membrane. However, with increase in pH, the membrane tends to become negative and is favorable for attracting MB molecule. Thus, the basic pH is preferable for adsorbing MB molecule on PVA/CMC/halloysite nanoclay membrane.

Adsorption isotherm

The adsorbate-adsorbent interaction and sorption capacity of the membrane were evaluated by using three different adsorption models namely Langmuir, Freundlich and Temkin. The linearized form of Langmuir isotherm is given below

$$\frac{C_e}{q_e} = \left(\frac{C_e}{q_{\max}} \right) + \left(\frac{1}{K_L * q_{\max}} \right) \quad (3)$$

Here, C_e (mgL⁻¹), q_e (mgg⁻¹) and $q_{\max}$ (mgg⁻¹) represent the equilibrium concentration of adsorbate, amount of adsorbate adsorbed at equilibrium and amount of analyte adsorbed per gram of adsorbent (or maximum adsorption capacity) respectively. K_L (L/g) is Langmuir sorption equilibrium constant which is related to the rate of adsorption and is mathematically defined as

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

Fig. 4 Effect of: **a** halloysite nanoclay dosage; **b** contact time; **c** initial concentration on MB; **d** temperature and **e** pH on PVA/CMC/halloysite nanoclay membrane

Here R_L (or separation factor) is a dimensional parameter which is related to the favorability of adsorption process. Adsorption is considered to be favorable if the R_L value falls between 0 and 1 and unfavorable if R_L is greater than 1. Validity of Langmuir model is tested by fitting the experimental data into Langmuir equation. The maximum adsorption capacity $q_{\max}$ and Langmuir constants K_L were obtained from the slope ($1/q_{\max}$) and intercept ($1/K_L q_{\max}$) of the plot C_e/q_e versus C_e .

The logarithmic form of Freundlich isotherm is represented as follows;

$$\ln(q_e) = \ln K_F + \frac{1}{n} \ln(C_e) \quad (5)$$

Here, K_F and n represent Freundlich constants. By plotting $\ln q_e$ vs $\ln C_e$ a straight line is obtained with $1/n$ as slope and $\ln K_F$ as intercept. K_F and n is related to the adsorption capacity

Scheme 1 Methylene blue adsorption on PVA/CMC membrane with different percentage of halloysite nanoclay

and adsorption intensity respectively and is used to predict the favorability of the adsorption process. If the value of n is between 1 and 10, then adsorption is considered favorable whereas a value below 1 is considered as an unfavorable.

The linearized form of Temkin is represented as,

$$B = B \ln A_T + B \ln C_e \quad (6)$$

Where $B = \frac{RT}{B_T}$ is temperature constant related to the heat of adsorption (J mol^{-1}). If $B > 0$, the process is said to be exothermic while a low value ($B < 0$) implies the endothermic nature of adsorption. A_T is Temkin isotherm constant (L/g) which is related to the binding energy, R is universal gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$) and T is absolute temperature in kelvin. From the

Fig. 5 UV-vis spectra of MB dye at different time interval (Photographs shown in inset corresponds to MB solution before and after adsorption)

Fig. 6 a Langmuir and b Freundlich isotherm and c Temkin plots for the MB adsorption onto PVA/CMC/halloysite nanoclay membrane

linear plot of q_e versus $\ln C_e$, the value of B (slope) and A_T (intercept) can be determined [6].

In order to understand the dye adsorption mechanism, we have fitted the equilibrium adsorption data into these isotherm models and the linear plot so obtained is displayed in Fig. 6. The values of isotherm constants and correlation coefficient (R^2) calculated using linear regression method are listed in Table 2. By comparing the linear plots of three isotherm models it is clear that Langmuir and Freundlich models give a better fit for adsorption of MB on membrane with high correlation coefficient ($R^2 = 0.98$ and

0.99). It can be also noted that the R_L value comes in the range of 0 and 1, thus suggesting that adsorption process is favorable [49].

Adsorption kinetics

The kinetics of MB adsorption on the PVA/CMC/halloysite nanoclay membrane were analyzed by applying pseudo-first (PFO), pseudo-second (PSO) and intraparticle diffusion models to the theoretical data [5, 96].

Table 2 Langmuir, Freundlich and Temkin isotherm parameters on PVA/CMC/halloysite nanoclay membrane

Experimental			Langmuir model			Freundlich model			Temkin model	
$q_{e, \text{exp.}} (\text{mg g}^{-1})$	$q_m (\text{mg g}^{-1})$	K_L	R_L	R^2	$K_F (\text{mg g}^{-1})$	n	R^2	$A_T (\text{L g}^{-1})$	B	R^2
8.29	40.6	1.58	0.059	0.98	7.5	1.1	0.999	1.1	28.5	0.937

Fig. 7 The linear plot of pseudo-first, pseudo-second and intraparticle diffusion models for MB adsorption onto PVA/CMC/halloysite nanoclay membrane

PFO model assumes physical interaction between adsorbate and adsorbent. The differential rate equation for the PFO kinetic model is given below;

$$\frac{dq_t}{dt} = K_1(q_e - q_t)$$

where the amounts of adsorbate adsorbed at 't' time and equilibrium respectively are represented as q_t (mg g^{-1}) and q_e (mg g^{-1}). The integrated form of equation is expressed as follows

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (7)$$

If the adsorption follows PFO model, then plot of $\log(q_e - q_t)$ vs time gives a straight line with slope K_1 and intercept q_e .

According to PSO kinetic model, adsorbate is chemically attracted to the adsorbent. The differential form of PSO model is expressed as

$$\frac{dq_t}{dt} = K_1(q_e - q_t)^2$$

where K_1 is the pseudo-first order rate constant. The linearized form of PSO model is denoted as

$$\frac{t}{q_e} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

Table 3 Adsorption kinetic parameters of MB on PVA/CMC/halloysite nanoclay membrane

Exp	Pseudo-first-order				Pseudo-second-order				Intra-particle diffusion		
	K_1 (min^{-1})	q_e (mg g^{-1})	R^2		K_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	q_e (mg g^{-1})	R^2		K_{id} ($\text{g mg}^{-1} \text{min}^{-1/2}$)	C (mg g^{-1})	R^2
8.29	-0.030	3.14	0.984		0.234	9.5	0.997		0.47	1.85	0.88

Fig. 8 The Van't Hoff plot of PVA/CMC/halloysite nanoclay membrane

K_2 (g/mg min⁻¹) is the pseudo-second-order rate constant. The value of K_2 and q_e can be calculated from the slope and intercept of the plot t/q_t vs time.

According to the intraparticle diffusion model, the kinetics of adsorption involves diffusion of adsorbent into the pores of adsorbent and is represented as.

$$q_t = K_{id}t^{1/2} + C \quad (9)$$

where K_{id} (mg min^{1/2}/g) and C are intraparticle constants and is estimated from the slope and intercept of the plot between q_t vs $t^{1/2}$.

The experimental values of MB adsorption were fitted into PFO, PSO and intraparticle model (Fig. 7). The kinetic parameters such K_1 , K_2 and K_{id} were calculated and is tabulated in Table 3. Comparison of the linear plot indicates that the PFO and intraparticle model does not fit the data perfectly and the experimental adsorption capacity does not match with the value calculated using PFO and intraparticle diffusion model. Thus, it can be confirmed that these models are not suitable to explain the kinetic mechanism of MB adsorption on to the membrane [74, 75]. On the other hand, it is evident that the best fit is obtained using PSO model and the correlation coefficient is closer to unity in this case. Moreover, the closeness of experimental (8.29 mg g⁻¹) and calculated kinetic parameters (9.5 mg g⁻¹) suggests that adsorption of MB on membrane follows PSO kinetics [56, 71].

Thermodynamics studies

In order to better understand the adsorption process, we have carried out the thermodynamic investigation. MB adsorption

of PVA/CMC/halloysite nanoclay membrane was studied at three different temperature (303, 313 and 323 K). The thermodynamic parameters (ΔG , ΔH and ΔS) were calculated using the Eqs. 10 and 11.

$$\ln \frac{q_e}{C_e} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (10)$$

The Gibbs free energy (ΔG) can be evaluated using the equation:

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

Where T is absolute temperature in Kelvin (K), R is the universal gas constant (8.314 J/ mol/ K). ΔG is the free energy of sorption (kJ/mol), ΔS (J/mol) and ΔH (kJ/mol) are respectively the entropy and enthalpy of sorption.

From the slope and intercept of the linear plot $\ln K (q_e/C_e)$ vs $1/T$, the ΔH and ΔS were obtained (Fig. 8). The thermodynamic parameters for MB adsorption process is displayed in Table 4. It can be seen that the ΔG is negative at all the temperature range. The negative value of free energy indicates that the adsorption of MB onto the membrane is spontaneous and feasible. The enthalpy of the process is found to be negative, thus suggesting exothermic nature of adsorption. The negative

Table 4 Thermodynamics parameters for MB adsorption on PVA/CMC/halloysite nanoclay membrane

ΔG (kJ/mol)			ΔH (kJ/mol)	ΔS (J/mol)
303 K	313 K	323 K		
-12.89	-10.38	-7.43	-46	-111

Fig. 9 Photographs of the antimicrobial activity of PVA/CMC/halloysite nanoclay membrane on **a** gram-positive (*Escherichia coli*) and **b** gram-negative (*Staphylococcus aureus*) bacteria: I) PCC-0 II) PCC-1 III) PCC-2 IV) PCC-3

value of ΔS indicate rearrangement of adsorption on the surfaces of PVA/CMC/halloysite nanoclay membrane [31].

Antimicrobial studies

The antimicrobial activity of synthesized membrane was identified by exposing it to two different bacteria such as *Escherichia coli* (gram-positive) and *Staphylococcus aureus* (gram-negative). The photographs obtained by inhibition zone method is shown in Fig. 9. It is clear from Fig. 9 that the membrane loaded with nanoclay inhibit the growth of gram-positive bacteria. However, its inhibition action toward gram-negative bacteria is very weak. We presume that the negative charge of clay inhibits the growth of gram-positive bacteria by

interacting electrostatically with its cell wall. Perhaps, electrostatic repulsion between gram-negative bacteria and clay could be the reason for the absence of clear inhibition zone. Based on this study, we can conclude that halloysite nanoclay loaded membrane possess antibacterial property and thus could be a potential candidate for water treatment.

Reusability

For practical application, an adsorbent with good recyclability is preferred. This prompted us to investigate the recyclability of PVA/CMC/halloysite nanoclay membrane. The desorption studies (Fig. 10) revealed that the even after four repeated recycle the membrane possesses high removal efficiency

Fig. 10 Reusability test on PVA/CMC/halloysite nanoclay membrane

Table 5 Recycle property of different adsorbent for removal of MB dye

Adsorbents	% removal	References
4A/PVA MMA	87	[13]
Keratin nanofibrous membrane	97	[11]
Potato leaves powder	85	[37]
Clay based adsorbent	70	[60]
Brown macroalga	70	[26]
Sugarcane bagasse	78	[97]
Wasted tea powder	73	[42]
PVA/CMC/halloysite nanoclay	90	This work

(88%). Table 5 displayed the recyclability of the membrane with other adsorbents (Table 5). From the table it is clear that our membrane possesses good recyclability and is much better than other adsorbents.

Conclusion

In summary, PVA/CMC/halloysite nanoclay membrane for removing MB from aqueous medium was successfully developed by solvent casting method. The adsorption studies indicate that the dye uptake capacity of the membrane could be tuned by experimental conditions such as nano clay dosage, initial concentration of MB, contact time, temperature and pH. The equilibrium adsorption data is well represented by both Langmuir and Freundlich model. Meanwhile, the pseudo-second-order model is found to be more suitable to describe the adsorption process. Thermodynamic studies revealed that the adsorption is spontaneous and exothermic in nature. The agar disc diffusion method confirmed the antibacterial activity of the membrane. Furthermore, the membrane possesses good reusability, which is beneficial for water treatment process.

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Compliance with ethical standards

Conflict of interest The authors don't have any conflicts of interests.

References

- Acher A, Fischer E, Turnheim R, Manor Y. Ecologically friendly wastewater disinfection techniques. *Water Res.* 1997;31(6):1398–404.
- Adeyemo AA, Adeoye IO, Bello OS. Adsorption of dyes using different types of clay: a review. *Appl Water Sci.* 2015;7(2):543–68.
- Afroze S, Sen TK, Ang M, Nishioka H. Adsorption of methylene blue dye from aqueous solution by novel biomass Eucalyptus sheathianabark: equilibrium, kinetics, thermodynamics and mechanism. *Desalin Water Treat.* 2015;57(13):5858–88.
- Afshin S, Mokhtari SA, Vosoughi M, Sadeghi H, Rashtbari Y. Data of adsorption of basic blue 41 dye from aqueous solutions by activated carbon prepared from filamentous algae. *Data Brief.* 2018;21:1008–13.
- Afshin S, Rashtbari Y, Ramavandi B, Fazlzadeh M, Vosoughi M, Mokhtari SA, et al. Magnetic nanocomposite of filamentous algae activated carbon for efficient elimination of cephalixin from aqueous media. *Korean J Chem Eng.* 2020;37(1):80–92.
- Ahmadi E, Kakavandi B, Azari A, Izanloo H, Gharibi H, Mahvi AH, et al. The performance of mesoporous magnetite zeolite nanocomposite in removing dimethyl phthalate from aquatic environments. *Desalin Water Treat.* 2016;1–15.
- Ahmadi E, Yousefzadeh S, Ansari M, Ghaffari HR, Azari A, Miri M, et al. Performance, kinetic, and biodegradation pathway evaluation of anaerobic fixed film fixed bed reactor in removing phthalic acid esters from wastewater. *Sci Rep.* 2017;7(1).
- Ali I, Asim M, Khan TA. Low cost adsorbents for the removal of organic pollutants from wastewater. *J Environ Manag.* 2012;113:170–83.
- Alipour M, Vosoughi M, Mokhtari SA, Sadeghi H, Rashtbari Y, Shirmardi M, et al. Optimising the basic violet 16 adsorption from aqueous solutions by magnetic graphene oxide using the response surface model based on the box–Behnken design. *Int J Environ Anal Chem.* 2019:1–20.
- Alizadeh S, Sadeghi H, Vosoughi M, Dargahi A, Mokhtari SA. Removal of humic acid from aqueous media using Sono-Persulphate process: optimization and modelling with response surface methodology (RSM). *Int J Environ Anal Chem.* 2020:1–15.
- Aluigi A, Rombaldoni F, Tonetti C, Jannoke L. Study of methylene blue adsorption on keratin nanofibrous membranes. *J Hazard Mater.* 2014;268:156–65.
- Aravind P, Selvaraj H, Ferro S, Sundaram M. An integrated (electro- and bio-oxidation) approach for remediation of industrial wastewater containing azo-dyes: understanding the degradation mechanism and toxicity assessment. *J Hazard Mater.* 2016;318:203–15.
- Baheri B, Ghahremani R, Peydayesh M, Shahverdi M, Mohammadi T. Dye removal using 4A-zeolite/polyvinyl alcohol mixed matrix membrane adsorbents: preparation, characterization, adsorption, kinetics, and thermodynamics. *Res Chem Intermed.* 2015;42(6):5309–28.
- Banerjee S, Chattopadhyaya MC. Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by-product. *Arab J Chem.* 2017;10:S1629–38.
- Barbosa AD, da Silva LF, de Paula HM, Romualdo LL, Sadoyama G, Andrade LS. Combined use of coagulation (M. oleifera) and electrochemical techniques in the treatment of industrial paint wastewater for reuse and/or disposal. *Water Res.* 2018;145:153–61.
- Bayat M, Javanbakht V, Esmaili J. Synthesis of zeolite/nickel ferrite/sodium alginate bionanocomposite via a co-precipitation technique for efficient removal of water-soluble methylene blue dye. *Int J Biol Macromol.* 2018;116:607–19.
- Bediako EG, Nyankson E, Dodoo-Arhin D, Agyei-Tuffour B, Łukowiec D, Tomiczek B, et al. Modified halloysite nanoclay as a vehicle for sustained drug delivery. *Heliyon.* 2018;4(7):e00689.

18. Bhardwaj A, Hossain SKS, Majhi MR. Preparation and characterization of clay bonded high strength silica refractory by utilizing agriculture waste. *Bol Soc Esp Ceram V*. 2017;56(6):256–62.
19. Bhatti HN, Safa Y, Yakout SM, Shair OH, Iqbal M, Nazir A. Efficient removal of dyes using carboxymethyl cellulose/alginate/polyvinyl alcohol/rice husk composite: adsorption/desorption, kinetics and recycling studies. *Int J Biol Macromol*. 2020;150:861–70.
20. Bielska M, Szymanowski J. Removal of methylene blue from waste water using micellar enhanced ultrafiltration. *Water Res*. 2006;40(5):1027–33.
21. Bouaziz F, Koubaa M, Kallel F, Chaari F, Driss D, Ghorbel RE, et al. Efficiency of almond gum as a low-cost adsorbent for methylene blue dye removal from aqueous solutions. *Ind Crop Prod*. 2015;74:903–11.
22. Castronovo S, Wick A, Scheurer M, Nödl K, Schulz M, Ternes TA. Biodegradation of the artificial sweetener acesulfame in biological wastewater treatment and sandfilters. *Water Res*. 2017;110:342–53.
23. Che Ramli ZA, Asim N, Isahak WNRW, Emdadi Z, Ahmad-Ludin N, Yarmo MA, et al. Photocatalytic degradation of methylene blue under UV light irradiation on prepared CarbonaceousTiO₂. *Sci World J*. 2014;2014:1–8.
24. Chen Y, Zhang Y, Liu J, Zhang H, Wang K. Preparation and antibacterial property of polyethersulfone ultrafiltration hybrid membrane containing halloysite nanotubes loaded with copper ions. *Chem Eng J*. 2012;210:298–308.
25. Dai H, Huang Y, Huang H. Eco-friendly polyvinyl alcohol/carboxymethyl cellulose hydrogels reinforced with graphene oxide and bentonite for enhanced adsorption of methylene blue. *Carbohydr Polym*. 2018;185:1–11.
26. Daneshvar E, Vazirzadeh A, Niazi A, Kousha M, Naushad M, Bhatnagar A. Desorption of methylene blue dye from brown macroalgae: effects of operating parameters, isotherm study and kinetic modeling. *J Clean Prod*. 2017;152:443–53.
27. Diagboya PN, Dikio ED. Scavenging of aqueous toxic organic and inorganic cations using novel facile magneto-carbon black-clay composite adsorbent. *J Clean Prod*. 2018;180:71–80.
28. Duman O, Polat TG, Diker CÖ, Tunç S. Agar/k-carrageenan composite hydrogel adsorbent for the removal of methylene blue from water. *Int J Biol Macromol*. 2020;160:823–35.
29. Edathil AA, Pal P, Banat F. Alginate clay hybrid composite adsorbents for the reclamation of industrial lean methyldiethanolamine solutions. *Appl Clay Sci*. 2018;156:213–23.
30. El Shahawy A, Heikal G. Organic pollutants removal from oily wastewater using clean technology economically, friendly biosorbent (*Phragmites australis*). *Ecol Eng*. 2018;122:207–18.
31. El-Shamy AG. An efficient removal of methylene blue dye by adsorption onto carbon dot @ zinc peroxide embedded poly vinyl alcohol (PVA/CZnO₂) nano-composite: a novel reusable adsorbent. *Polymer*. 2020;202:122565.
32. Falcón JM, Sawczen T, Aoki IV. Dodecylamine-loaded halloysite nanocontainers for active anticorrosion coatings. *Front Mater*. 2015;2.
33. Farzadnia N, Abang Ali AA, Demirboga R, Anwar MP. Effect of halloysite nanoclay on mechanical properties, thermal behavior and microstructure of cement mortars. *Cement and Concrete Research*. 2013;48:97–104.
34. Goluboff N, Wheaton R. Methylene blue induced cyanosis and acutemolytic anemia complicating the treatment of methemoglobinemia. *J Pediatr*. 1961;58(1):86–9.
35. Gu S, Kang X, Wang L, Lichtfouse E, Wang C. Clay mineral adsorbents for heavy metal removal from wastewater: a review. *Environ Chem Lett*. 2018;17(2):629–54.
36. Güler M, Çetintaş S, Bingöl D. Cinnamon bark as low-cost and eco-friendly adsorbent for the removal of indigo carmine and malachite green dyestuffs. *Int J Environ Anal Chem*. 2019:1–23.
37. Gupta N, Kushwaha AK, Chattopadhyaya MC. Application of potato (*Solanum tuberosum*) plant wastes for the removal of methylene blue and malachite green dye from aqueous solution. *Arab J Chem*. 2016;9:S707–16.
38. Hajjaji W, Pullar RC, Labrincha JA, Rocha F. Aqueous acid Orange 7 dye removal by clay and red mud mixes. *Appl Clay Sci*. 2016;126:197–206.
39. Hameed BH, Ahmad AL, Latiff KNA. Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. *Dyes Pigments*. 2007;75(1):143–9.
40. Haouzi P, Gueguinou M, Sonobe T, Judenherc-Haouzi A, Tubbs N, Trebak M, et al. Revisiting the physiological effects of methylene blue as a treatment of cyanide intoxication. *Clin Toxicol*. 2018;56(9):828–40.
41. Hu L, He K, Chen G, Zeng G, Chen A, Huang Z, Shi J, Peng M, Huang T. Enhanced removal performance for methylene blue by kaolin with graphene oxide modification. *J Taiwan Inst Chem Eng*. 2018; 1–9.
42. Hu Y, Zhang Y, Hu Y, Chu C-Y, Lin J, Gao S, et al. Application of wasted oolong tea as a biosorbent for the adsorption of methylene blue. *J Chem*. 2019;2019:1–10.
43. Jaseela PK, Garvasis J, Joseph A. Selective adsorption of methylene blue (MB) dye from aqueous mixture of MB and methyl orange (MO) using mesoporous titania (TiO₂) – poly vinyl alcohol (PVA) nanocomposite. *J Mol Liq*. 2019;286:110908.
44. Jawad AH, Abdulhameed AS. Mesoporous Iraqi red kaolin clay as an efficient adsorbent for methylene blue dye: adsorption kinetic, isotherm and mechanism study. *Surf Interfaces*. 2020;18:100422.
45. Kapadia K, Cheung F, Lee W, Thalappillil R, Florence FB, Kim J. Methylene blue causing serotonin syndrome following cystocele repair. *Urol Case Rep*. 2016;9:15–7.
46. Karcher S, Kornmüller A, Jekel M. Anion exchange resins for removal of reactive dyes from textile wastewaters. *Water Res*. 2002;36(19):4717–24.
47. Kausar A, Iqbal M, Javed A, Aftab K, Nazli ZIH, Bhatti HN, et al. Dyes adsorption using clay and modified clay: a review. *J Mol Liq*. 2018;256:395–407.
48. Kiernan JA. Dyes and other colorants in microtechnique and biomedical research. *Color Technol*. 2006;122(1):1–21.
49. Kundu A, Mondal A. Kinetics, isotherm, and thermodynamic studies of methylene blue selective adsorption and photocatalysis of malachite green from aqueous solution using layered Na-intercalated Cu-doped Titania. *Appl Clay Sci*. 2019;183:105323.
50. Kuroda S, Nagaishi T, Kameyama M, Koido K, Seo Y, Dowaki K. Hydroxyl aluminium silicate clay for biohydrogen purification by pressure swing adsorption: physical properties, adsorption isotherm, multicomponent breakthrough curve modelling, and cycle simulation. *Int J Hydrog Energy*. 2018;43(34):16573–88.
51. Lellis B, Fávoro-Polonio CZ, Pamphile JA, Polonio JC. Effects of textile dyes on health and the environment and bioremediation potential of living organisms. *Biotechnol Res Innov*. 2019;3(2): 275–90.
52. Liu S, Ding Y, Li P, Diao K, Tan X, Lei F, et al. Adsorption of the anionic dye Congo red from aqueous solution onto natural zeolites modified with N,N-dimethyl dehydroabietylamine oxide. *Chem Eng J*. 2014;248:135–44.
53. Liu C, Omer AM, Ouyang X-K. Adsorptive removal of cationic methylene blue dye using carboxymethyl cellulose/k-carrageenan/activated montmorillonite composite beads: isotherm and kinetic studies. *Int J Biol Macromol*. 2018;106:823–33.
54. Lopes TJ, Gonçalves OH, Barros RB, Capelli FCR, Machado RAF, Quadri MGN, et al. Adsorption of natural dyes on clay fixed on polymers. *Braz Arch Biol Technol*. 2005;48(spe):275–80.

55. Mahbub MKB, Begum HA. Effectiveness of carboxymethyl cellulose for the removal of methylene blue from aqueous solution. *Dhaka Univ J Sci*. 2013;61(2):193–8.
56. Mallakpour S, Tabesh F. Tragacanth gum based hydrogel nanocomposites for the adsorption of methylene blue: comparison of linear and non-linear forms of different adsorption isotherm and kinetics models. *Int J Biol Macromol*. 2019;133:754–66.
57. Mirakbari SM. Methylene blue unresponsive methemoglobinemia. *Indian J Crit Care Med*. 2014;18(7):483–4.
58. Moazzen M, Mousavi Khaneghah A, Shariatifar N, Ahmadloo M, Eş I, Baghani AN, et al. Multi-walled carbon nanotubes modified with iron oxide and silver nanoparticles (MWCNT-Fe₃O₄/Ag) as a novel adsorbent for determining PAEs in carbonated soft drinks using magnetic SPE-GC/MS method. *Arab J Chem*. 2019;12(4):476–88.
59. Momina M, Shahadat M, Isamil S. Regeneration performance of clay-based adsorbents for the removal of industrial dyes: a review. *RSC Adv*. 2018;8(43):24571–87.
60. Momina, Rafatullah M, Ismail S, Ahmad A. Optimization study for the desorption of methylene blue dye from clay based adsorbent coating. *Water*. 2019;11(6):1304.
61. Nagendrappa G. Organic synthesis using clay and clay-supported catalysts. *Appl Clay Sci*. 2011;53(2):106–38.
62. Peng Z, Guo Z, Chu W, Wei M. Facile synthesis of high-surface-area activated carbon from coal for supercapacitors and high CO₂ sorption. *RSC Adv*. 2016;6(48):42019–28.
63. Pimneva L, Zagorskaya A. Modification of natural clays for use in the processes of sewage treatment. *J Ecol Eng*. 2019;20(8):12–7.
64. Radoor S, Karayil J, Parameswaranpillai J, Siengchin S. Adsorption study of anionic dye, Eriochrome black T from aqueous medium using polyvinyl alcohol/starch/ZSM-5 zeolite membrane. *J Polym Environ*. 2020;28(10):2631–43.
65. Rafatullah M, Sulaiman O, Hashim R, Ahmad A. Adsorption of methylene blue on low-cost adsorbents: a review. *J Hazard Mater*. 2010;177(1–3):70–80.
66. Ramadass K, Singh G, Lakhi KS, Benzigar MR, Yang JH, Kim S, et al. Halloysite nanotubes: novel and eco-friendly adsorbents for high-pressure CO₂ capture. *Microporous Mesoporous Mater*. 2019;277:229–36.
67. Ramesh S, Punithamoorthy K. Synthesis, characterization and gas permeability properties of a novel nanocomposite based on poly(ethylene-co-vinyl acetate)/polyurethane acrylate/clay. *J Mater Res Technol*. 2019;8(5):4173–81.
68. Rasalingam S, Peng R, Koodali RT. Removal of hazardous pollutants from wastewaters: applications of TiO₂-SiO₂ Mixed oxide materials. *J Nanomater*. 2014;2014:1–42.
69. Rida K, Bouraoui S, Hadnine S. Adsorption of methylene blue from aqueous solution by kaolin and zeolite. *Applied Clay Science*. 2013;83–84:99–105.
70. Rizzi V, Prasetyanto EA, Chen P, Gubitosa J, Fini P, Agostiano A, et al. Amino grafted MCM-41 as highly efficient and reversible ecofriendly adsorbent material for the direct blue removal from wastewater. *J Mol Liq*. 2019;273:435–46.
71. Roghanizad A, Abdolmaleki MK, Ghoreishi SM, Dinari M. One-pot synthesis of functionalized mesoporous fibrous silica nanospheres for dye adsorption: isotherm, kinetic, and thermodynamic studies. *J Mol Liq*. 2020;300:112367.
72. Sabarish R, Unnikrishnan G. Synthesis, characterization and catalytic activity of hierarchical ZSM-5 templated by carboxymethyl cellulose. *Powder Technol*. 2017;320:412–9.
73. Sabarish R, Unnikrishnan G. Novel biopolymer templated hierarchical silicalite-1 as an adsorbent for the removal of rhodamine B. *J Mol Liq*. 2018a;272:919–29.
74. Sabarish R, Unnikrishnan G. Polyvinyl alcohol/carboxymethyl cellulose/ZSM-5 zeolite biocomposite membranes for dye adsorption applications. *Carbohydr Polym*. 2018b;199:129–40.
75. Sabarish R, Unnikrishnan G. PVA/PDADMAC/ZSM-5 zeolite hybrid matrix membranes for dye adsorption: fabrication, characterization, adsorption, kinetics and antimicrobial properties. *J Environ Chem Eng*. 2018c;6(4):3860–73.
76. Sabarish R, Unnikrishnan G. Synthesis, characterization and evaluations of micro/mesoporous ZSM-5 zeolite using starch as bio template. *SN Appl Sci*. 2019;1(9).
77. Sabarish R, Unnikrishnan G. A novel anionic surfactant as template for the development of hierarchical ZSM-5 zeolite and its catalytic performance. *J Porous Mater*. 2020;27(3):691–700.
78. Sabir A, Falath W, Jacob KI, Shafiq M, Gull N, Islam A, et al. Integrally skinned nano-cellular crosslinked asymmetric thin films infused with PEO-PPO-PEO block copolymer/ZnO-NPs for desalination using sea salt. *Mater Chem Phys*. 2016;183:595–605.
79. Saharudin MS, Atif R, Shyha I, Inam F. The degradation of mechanical properties in halloysite nanoclay–polyester nanocomposites exposed to diluted methanol. *Journal of Composite Materials*. 2016;51(11):1653–64.
80. Salima A, Ounissa K-S, Lynda M, Mohamed B. Cationic dye (MB) removal using polymer inclusion membrane (PIMs). *Procedia Eng*. 2012;33:38–46.
81. Samarghandi MR, Dargahi A, Shabanloo A, Nasab HZ, Vaziri Y, Ansari A. Electrochemical degradation of methylene blue dye using a graphite doped PbO₂ anode: optimization of operational parameters, degradation pathway and improving the biodegradability of textile wastewater. *Arab J Chem*. 2020a;13(8):6847–64.
82. Samarghandi MR, Dargahi A, Zolghadr Nasab H, Ghahramani E, Salehi S. Degradation of azo dye acid red 14 (AR14) from aqueous solution using H₂O₂/nZVI and S₂O₈²⁻/nZVI processes in the presence of UV irradiation. *Water Environ Res*. 2020b;92(8):1173–83.
83. Somsesta N, Sricharoenchaiikul V, Aht-Ong D. Adsorption removal of methylene blue onto activated carbon/cellulose biocomposite films: equilibrium and kinetic studies. *Mater Chem Phys*. 2020;240:122221.
84. Srinivasan R. Advances in application of natural clay and its composites in removal of biological, organic, and inorganic contaminants from drinking water. *Adv Mater Sci Eng*. 2011;2011:1–17.
85. Thirumoorthy K, Krishna SK. Preparation and characterization of ball clay-manganese dioxide Nanocomposites. *Asian J Chem*. 2019;31(1):83–8.
86. Ting Z, Zhiyuan P. Bio-adsorbent from Carboxymethyl cellulose and tannin for dye adsorption. *J Macromol Sci B*. 2018;57(3):177–86.
87. Uddin MK. A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. *Chem Eng J*. 2017;308:438–62.
88. Wang S, Li H, Xie S, Liu S, Xu L. Physical and chemical regeneration of zeolitic adsorbents for dye removal in wastewater treatment. *Chemosphere*. 2006;65(1):82–7.
89. Wang Q, Ju J, Tan Y, Hao L, Ma Y, Wu Y, et al. Controlled synthesis of sodium alginate electrospun nanofiber membranes for multi-occasion adsorption and separation of methylene blue. *Carbohydr Polym*. 2019a;205:125–34.
90. Wang X, Mu B, Wang W, Wang Q, Wang A. A comparative study on color properties of different clay minerals/BiVO₄ hybrid pigments with excellent thermal stability. *Appl Clay Sci*. 2019b;181:105221.
91. Wei W, Abdullayev E, Hollister A, Mills D, Lvov YM. Clay nanotube/poly(methyl methacrylate) bone cement composites with sustained antibiotic release. *Macromol Mater Eng*. 2012;297(7):645–53.
92. Wong S, Yac'cob NAN, Ngadi N, Hassan O, Inuwa IM. From pollutant to solution of wastewater pollution: synthesis of activated carbon from textile sludge for dye adsorption. *Chin J Chem Eng*. 2018;26(4):870–8.

93. Xue Y, Xiang P, Wang H, Jiang Y, Long Y, Lian H, et al. Mechanistic insights into selective adsorption and separation of multi-component anionic dyes using magnetic zeolite imidazolate framework-67 composites. *J Mol Liq*. 2019;296:111990.
94. Yegane Badi M, Vosoughi M, Sadeghi H, Mokhtari SA, Mehralipour J. Ultrasonic-assisted H₂O₂/TiO₂ process in catechol degradation: kinetic, synergistic and optimisation via response surface methodology. *Int J Environ Anal Chem*. 2020:1–14.
95. Yin X, Wang L, Li S, He G, Yang Z. Effects of surface modification of halloysite nanotubes on the morphology and the thermal and rheological properties of polypropylene/halloysite composites. *J Polym Eng*. 2018;38(2):119–27.
96. Yousefzadeh S, Ahmadi E, Gholami M, Ghaffari HR, Azari A, Ansari M, et al. A comparative study of anaerobic fixed film baffled reactor and up-flow anaerobic fixed film fixed bed reactor for biological removal of diethyl phthalate from wastewater: a performance, kinetic, biogas, and metabolic pathway study. *Biotechnol Biofuels*. 2017;10(1):139.
97. Yu J-X, Chi RA, Guo J, Zhang YF, Xu ZG, Xiao CQ. Desorption and photodegradation of methylene blue from modified sugarcane bagasse surface by acid TiO₂ hydrosol. *Appl Surf Sci*. 2012;258(8):4085–90.
98. Zhang T, Oyama T, Aoshima A, Hidaka H, Zhao J, Serpone N. Photooxidative N-demethylation of methylene blue in aqueous TiO₂ dispersions under UV irradiation. *J Photochem Photobiol A Chem*. 2001;140(2):163–72.
99. Zhu T, Tao Z, Jia L, Luo YF, Xu J, Chen RH, et al. Multifunctional nanocomposite based on halloysite nanotubes for efficient luminescent bioimaging and magnetic resonance imaging. *Int J Nanomedicine*. 2016;11:4765–76.
100. Zhu J, Li Q, Che Y, Liu X, Dong C, Chen X, et al. Effect of Na₂CO₃ on the microstructure and macroscopic properties and mechanism analysis of PVA/CMC composite film. *Polymers*. 2020;12(2).

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