Synthesis of an efficient hydroxyapatite–chitosan–montmorillonite thin film for the adsorption of anionic and cationic dyes: adsorption isotherm, kinetic and thermodynamic study

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Abstract

Adsorption of indigo carmine (IC), methyl orange (MO) and methylene blue (MB) onto hydroxyapatite–chitosan–montmorillonite (HAP–CTS–Mt) film was studied. The influence of contact time, solution pH, initial dyes concentration, amount of HAP–CTS–Mt film and solution temperature were scrutinized. Characteristic bands and structure of HAP–CTS–Mt film were determined using Fourier infrared spectroscopy and X-ray diffraction. The optimal concentrations of IC, MO, and MB were 20 mg/L, 50 mg/L, and 20 mg/L, respectively. Optimal dose of HAP–CTS–Mt was 0.2 g/L for IC and MB and 0.5 g/L for MO. The adsorption process of IC, MO, and MB using HAP–CTS–Mt film was verified by Langmuir isotherm model with maximum adsorption capacities of 243.18 mg/g, 137.5 mg/g and 168.52 mg/g for IC, MO, and MB, respectively. The adsorption kinetics of IC, MO, and MB onto HAP–CTS–Mt film were well fitted by the pseudo-second-order model. The HAP–CTS–Mt thin film can be employed as an efficient adsorbent for removal of IC, MO, and MB dyes from aqueous solutions.

Keywords Adsorption · Hydroxyapatite–chitosan–montmorillonite film · Anionic dye · Cationic dye · Adsorption kinetics · Adsorption isotherms

1 Introduction

Recently, the treatment of industrial wastewater, particularly in textile and chemical industries has been getting increasing attention [1–4]. A very small amount of dye in water is highly visible and toxic to aquatic life; dye effluents do not only distress the aquatic system, it also inhibits the transmittance of light into water which harms the ecosystem [5–8]. Therefore, the removal of dyes using different processes became a fundamental concern for the environment.

Several techniques have been applied to manage dyes effluents [9]. Adsorption processes remain the preferred technique for the decontamination of effluents from

textile and dyeing industries [10–15] due to its simplicity and cost-effectiveness compared to other methods (coagulation and flocculation [16], ozonation [17], membrane [12], electrochemical [18, 19], fungal discoloration [20].

Chitosan (CTS) has been employed as an adsorbent in wastewater treatment in many studies [21, 22]. However, it has some limits regarding its solubility only attained in acidic medium. Many researchers have focused on adding inorganic materials to CTS, for example; calcium phosphates, hydroxyapatite (HAP) and montmorillonite (Mt) clay, the alteration of their structure can successfully improve their adsorption capabilities [23–27].

In this study, a mixture of HAP, CTS, and Mt was developed in the form of a thin film; the role of HAP in the

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HAP–CTS–Mt thin film was to stabilize CTS and provide adsorption sites by first adsorbing Ca^{2+} through the amino. Groups on the surface of the CTS and then by slowly reacting with PO_4^{3-} ions [28]. It was further tested for the adsorption of IC, MO, and MB and the effects of solution pH, temperature, dose of adsorbent and initial IC, MB, and MO concentrations were studied.

2 Materials and methods

2.1 Materials

Indigo Carmine dye (IC), chemical formula: $\text{C}_{16}\text{H}_8\text{O}_8\text{N}_2\text{S}_2\text{Na}_2$, FW: 466.36 g/mol, $\lambda_{\text{max}}=610$ nm was supplied by Rrolab. Methyl Orange dye (MO), chemical formula: $\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$, FW: 327.33 g/mol, $\lambda_{\text{max}}=464$ nm was supplied by Sigma Aldrich. The chemical formula of Methylene Blue (MB) is $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$, FW: 319.85 g/mol, $\lambda_{\text{max}}=670$ nm and was obtained from Sigma Aldrich. The Molecular formula of the chitosan used in this study is $\text{C}_{12}\text{H}_{24}\text{N}_2\text{O}_9$, FW: 100 KDa, (CTS, > 85% deacetylation) it was purchased from Sigma Aldrich. The montmorillonite Na^+ (Mt) was procured from Southern Clay Products, Inc. The composition of sodium montmorillonite particles is as follows (wt%): Na_2O :7.223, MgO : 4.133, Al_2O_3 :19.986, SiO_2 :56.851, P_2O_5 :0.022, K_2O :0.442, CaO :0.698, Mno. :0.053, TiO :0.368, Fe_2O_3 :7.936. Hydroxyapatite (HAP) $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ was synthesized from Moroccan phosphogypsum waste in our previous published study [29], this method leads to obtaining HAP with a (Ca/P)= 1.667 and with a high purity, its chemical compositions(wt%): Ca 33.45, P: 15.51, Na: 0.13, C: 0.21 and F 0.03. Mt, HAP, CTS and HAP–CTS–Mt thin film were characterized by X-ray diffraction using a diffractometer (XRD: BRUKER), Cu K α radiation ($\lambda=1.54$ Å) created at 40 kV, a scan range 2θ equal to $3\text{--}70^\circ$. These samples were also analyzed using an FT-IR spectrometer (Alpha Burkert) ranging from 373 to 4000 cm^{-1} .

2.2 Synthesis of HAP–CTS–Mt thin film

An initial chitosan solution was obtained by dissolving 3.5 g of chitosan in 0.1 L of a 0.1 M acetic acid solution. The dissolution was performed for 3 h with continuous stirring at room temperature. CTS–HAP suspension was formed by adding 0.4375 g HAP to CTS solution; the mixture was stirred for 24 h. 0.4375 g of Mt was dissolved separately in 30 mL deionized water and was stirred mechanically for 24 h. Both CTS–HAP and Mt solutions were mixed together thoroughly to form a gel, then spread out evenly on a glass surface and was left to dry in open air to form thin sheets.

2.3 Adsorption experiments

Batch adsorption study of IC, MO, and MB on HAP–CTS–Mt was conducted to investigate the effect of various operating parameters, including contact time (0–150 min), adsorbent dose (0–1 g/L), solution pH (4–10), initial IC, MO and MB concentrations (0–200 mg/L) and solution temperature (293–333 K). A specific amount of HAP–CTS–Mt was added in 100 ml of dye aqueous solution. The pH was adjusted using a few drops of 0.1 M HCl or 0.1 M NaOH. The adsorbed amounts of IC, MO, and MB were determined using Jasco V-630 UV visible spectrophotometer by measuring the absorbance at 610 nm, 464 nm, and 670 nm of IC, MO, and MB, respectively. The removal percentage of IC, MO, and MB onto HAP–CTS–Mt and the adsorption capacity at equilibrium (q_e) and at time (q_t) (mg/g) was determined by the following equations:

$$\% \text{Removal} = \frac{C_0 - C_e}{C_0} \times 100$$

$$q_e = \frac{C_0 - C_e}{M} \times V$$

$$q_t = \frac{C_0 - C_t}{m} \times V$$

where C_0 (mg/L) is the initial IC, MO and MB concentrations, C_t and C_e are the dye concentrations at time (t) and at equilibrium, m (g) is the amount of HAP–CTS–Mt and V (L) is the volume of the solution [30].

3 Results and discussion

3.1 Adsorbent characterization by XRD and FTIR

The XRD of CTS, Mt, HAP and HAP–CTS–Mt are presented in Fig. 1a. CTS powder diffractogram showed a peak at $2\theta=9.8^\circ$ assigned to (020) and another one at $2\theta=19.9^\circ$ which was attributed to (110) [31, 32]. The HAP diffractogram showed three peaks, two intense peaks at $2\theta=32^\circ$ which were assigned to (211) and (112) and one peak at $2\theta=33^\circ$ which was attributed to (300) [33].

The Mt XRD pattern displayed an overall crystalline structure showing peaks at $2\theta=6^\circ$ and $2\theta=20^\circ$ which were attributed to (001) and (100) planes corresponding to quartz which is commonly found in clays [34]. The HAP–CTS–Mt film spectra showed HAP basal peaks at $2\theta=32^\circ$ and 33° , which confirms the presence of the HAP molecule in the HAP–CTS–MT film. Also, Mt and CTS

Fig. 1 **a** XRD patterns and **b** FT-IR spectra of samples

characteristic peaks appeared at $2\theta = 20^\circ$, indicating the presence of CTS and Mt molecules in the HAP-CTS-Mt film. The basal peak of Mt had shifted from 6.2 to 5.0 , which changes the d_{001} from 14.23°A to 17.65°A . The 3.42°A increase in d_{001} indicates the formation of intercalated CTS-HAP/Mt structure. Scheme 1 presents the possible interactions between chitosan, Mt and HAP.

Figure 1b shows the FTIR spectra of HAP, CTS, Mt powders and HAP-CTS-Mt thin film. CTS IR spectra showed peaks at 3363 cm^{-1} assigned to O-H stretching band at 3284 cm^{-1} corresponding to N-H stretching band. However, the HAP-CTS-Mt film spectra exhibited a broader N-H stretching, indicating a protonation of amino groups of CTS by the overlapping of O-H large band with N-H. In addition, the N-H band of CTS powder had shifted from 1561 to 1536 cm^{-1} in HAP-CTS-Mt film [35]. The characteristic bands of C-O-C linkage were observed at 1150 cm^{-1} and 1034 cm^{-1} . The C-N band appeared at 898 cm^{-1} [36, 37]. The HAP spectra showed characteristic phosphate peaks at 1021 cm^{-1} and 961 cm^{-1} which shifted to the right in the HAP-CTS-Mt film spectra. CO_3^{2-} bands appeared at 1406 cm^{-1} . The N-H bending had also shifted from 1458 cm^{-1} to 1536 cm^{-1} in the HAP-CTS-Mt film due to interactions between the amide group of CTS and PO_4^{3-} of HAP [38, 39]. The FT-IR spectra of Mt showed elongating of O-H of H_2O at 3624 cm^{-1} . Bands at 3433 cm^{-1} and 1633 cm^{-1} were assigned to O-H stretching of H_2O . The band at 514 cm^{-1} was allocated to Si-O-Al deformation and the Si-O-Si band of Mt powder [40, 41]. FT-IR spectrum of HAP-CTS-Mt thin film showed similar characteristic band of the HAP, CTS and Mt with some shifts and with low intensity. The HAP-CTS-Mt spectrum showed similar bands to CTS spectra; this is due to the high amount of CTS in the HAP-CTS-Mt film. The analysis given above showed no destruction of materials during the film preparation.

Scheme 1 Schematic diagram of HAP-CTS-Mt thin film.

Fig. 2 Effect of contact time on the dye adsorption onto HAP-CTS-Mt thin film ($C_0=20$ mg/L for IC and MB, $C_0=50$ mg/L for MO, $m_{\text{HAP-CTS-Mt}}=0.2$ g/L for IC and MB, $m_{\text{HAP-CTS-Mt}}=0.5$ g/L for MO, $T=\text{room temperature}$)

4 Effect of contact time

Figure 2 indicates the adsorption capacities of IC, MO, and MB onto HAP-CTS-Mt as function of time. The adsorption capacity was relatively rapid in the first 5 min due to the higher number of vacant sites of HAP-CTS-Mt in the first minutes and then slowed down to reach equilibrium after 90 min, 60 min and 60 min of contact for IC, MO, and MB, respectively. At the equilibrium, the adsorption capacities were registered at 99.87 mg/g, 96.65 mg/g and 47.92 mg/g for IC, MO, and MB, respectively.

4.1 Effect of adsorbent amount

Figure 3 shows the effect of varying the adsorbent dosage from 0 to 1.5 g/L of HAP-CTS-Mt on the adsorption of the three dyes. At dosage less than 0.2 g/L for IC, MB and 0.5 g/L for MO, the removal percentages increased rapidly, and then became constant to achieve equilibrium at 0.2 g/L for IC and MB and 0.5 g/L for MO; due to the availability of free adsorption sites on the adsorbent surface [42]. Consequently, 0.2 g/L was chosen as the optimal dose for the adsorption of IC and MB, whereas, 0.5 g/L was considered as optimal dose for the adsorption of MO onto HAP-CTS-Mt. This difference of optimal dose can be attributed to the number of benzene in the dye structure as explained by Ocholi et al. [43].

Fig. 3 Effect of adsorbent dosage on the removal of dyes onto HAP-CTS-Mt thin film ($C_0=20$ mg/L for IC and MB and 50 mg/L for MO, pH=6 and $T=\text{room temperature}$ (293 K))

4.2 Effect of initial pH

The pH point zero charge (PZC) corresponds to the pH at which the HAP-CTS-Mt surface has no charge. The PZC was found to be 6.24 (see Fig. 4). This indicates that at pH values less than 6.24, the surface of HAP-CTS-Mt is positive while at pH values higher than 6.24, the surface of HAP-CTS-Mt is negatively charged. Hence the adsorption of dyes charged negatively was favorable at pH values around or under 6.24, whereas at pH values above 6.24, the adsorption of dyes charged positively was effective (Fig. 4).

The low adsorption capacity of IC, MO and MB using HAP-CTS-Mt registered at pH=4 can be explained according to two hypotheses; first, the lower adsorption capacity may be due to the chitosan solubilization which happens for pHs lower than 6 [44]. Second, the pKa of MO and MB are 4.4–5.5 and 3.8 respectively, indicating that the MO and MB were protonated, that decrease the fixation of the MO and MB into HAP-CTS-Mt thin film [45, 46].

The removal rate of IC, MO and MB by HAP-CTS-Mt rapidly increased at pH values ranged from 5 to 6.24. However, adsorption capacities for IC and MO decreased by increasing pH from 8 to 10; creating electrostatic repulsion between the negatively charged surface of HAP-CTS-Mt and the anionic IC and MO molecules; this resulted in low adsorption capacities of IC and MO [47]. Contrariwise, for MB, the adsorption capacity rose by increasing pH; this is due to the negatively charged surface of HAP-CTS-Mt

Fig. 4 **a** Effect of pH on the removal of dyes onto HAP-CTS-Mt thin film ($C_0=20$ mg/L for IC and MB and 50 mg/L for MO, $m_{\text{HAP-CTS-Mt}}=0.2$ g/L for IC and MB, $m_{\text{HAP-CTS-Mt}}=0.5$ g/L for MO, and $T=\text{room temperature (293 K)}$, **b** the point zero charge of HAP-CTS-Mt

at pH values higher than 8, facilitating the association between the cationic charge of MB and the thin film.

4.3 Proposed adsorption mechanism

The adsorption mechanism of IC, MO and MB using HAP-CTS-Mt thin film can be interpreted by the electrostatic interactions between the negatively charged of IC, MO dyes and positively charged surface of HAP-CTS-Mt thin film at pH values less than 6.24. However, the adsorption of MB using this adsorbent can be conducted to electrostatic interactions between the positive charge of MB and negative charge of HAP-CTS-Mt at pH values higher than 6.24 (see Scheme 2).

4.4 Effect of initial dye concentration

The effect of initial IC, MO and MB dyes concentrations was studied from 10 to 200 mg/L (Fig. 5). It is observed that a rise in the initial IC, MO and MB dyes concentrations lead to a rise in the adsorption capacities, IC from 56 to 250 mg/g, MO from (19.42 to 137.48 mg/g) and MB from (39.63 to 157 mg/g). This is due to the rise in the driving force of the concentration gradient with enhancing the initial IC, MO and MB concentration [48–50].

4.5 Effect of temperature

The temperature of IC, MO and MB solutions was varied to test the effect of this factor on the adsorption phenomena (Fig. 6). A decrease from 99.29 to 89.5 mg/g, 96.63 to

79.44 mg/g and 45.04 to 40.1 mg/g of the adsorption capacity was observed for IC, MO, and MB respectively, as increasing temperature, indicating that the adsorption reaction was exothermic. Such behaviors may be due to the bonding between IC, MO, MB molecules and the active sites of HAP-CTS-Mt which weakened when the temperature increased [51].

4.6 Adsorption kinetics and isotherms study

The kinetic study provides important information about the mechanism of IC, MO and MB adsorption onto HAP-CTS-Mt. The kinetic parameters were determined using pseudo-first-order and pseudo-second-order equations [52–54] at optimum dose of HAP-CTS-Mt, pH, initial dyes concentration and temperature for batch adsorption process. The nonlinear equations of the two models are presented in Table 1. The most-fit model was selected from the nonlinear regression correlation coefficient values (R^2). The model parameters were evaluated using Origin 8.0 software. The main statistical criteria were the regression coefficient (R^2), and the chi-square analysis (χ^2) [54].

The adsorption capacities, constants rates, and regression coefficients are depicted in Table 2. The correlation coefficient close to unity, and experimental values for q_e are similar to the calculated ones (Table 2) indicate that the adsorption of IC, MO and MB using HAP-CTS-Mt is described by the pseudo-second-order model (See Fig. 7). In this work, three important isotherm models, namely Freundlich [55, 56], Langmuir [57–59] and Dubinin–Radushkevich [60] were studied; the Langmuir isotherm model

Scheme 2 Schematic diagram possible for the adsorption of IC, MO and MB using HAP-CTS-Mt thin film

is founded on the assumption of monolayer of molecules on the adsorbent surface. However, the Freundlich model shows the heterogeneity for adsorbate-adsorbent interactions, and the Dubinin–Radushkevich model is used to predict the physical or chemical nature of adsorption by calculating sorption energy. The equations describing the three isotherms models are listed in Table 1.

The isotherm constants for the Langmuir, the Freundlich and the Dubinin–Radushkevich isotherm models

have been calculated using nonlinear regression with the help of Origin (Version 8) software program. The results for the three isotherms models are presented in Fig. 8. The values of different parameters are presented in Table 3. The adsorption of the three dyes using the prepared film followed the Langmuir model. The values of R^2 of this model are superior to 0.98 for the studied dyes showing that the Langmuir model fits the adsorption process of IC, MO, and MB onto HAP-CTS-Mt. The E values are calculated to

Fig. 5 Effect of concentration on the removal of dyes onto HAP-CTS-Mt thin film ($m_{\text{HAP-CTS-Mt}}=0.2$ g/L for IC and MB, $m_{\text{HAP-CTS-Mt}}=0.5$ g/L for MO and $T=\text{room temperature (293 K)}$)

Fig. 6 Effect of temperature on the removal of dyes onto HAP-CTS-Mt thin film ($m_{\text{HAP-CTS-Mt}}=0.2$ g/L for IC and MB, $m_{\text{HAP-CTS-Mt}}=0.5$ g/L for MO and $C_0=20$ mg/L for IC and MB and 50 mg/L for MO)

determine the type of adsorption process. If $8 < E < 16$ kJ/mol, the adsorption process is a chemical adsorption, however, if $E < 8$ kJ/mol, the adsorption process is physical in nature. In this study, the values of the E determined from Dubinin–Radushkevich equation are < 8 kJ/mol, indicating that the adsorption of the IC, MO and MB by HAP-CTS-Mt is physical in nature.

4.7 Thermodynamic parameters

Section 3.7 revealed that the adsorption capacity decreases by increasing solution temperature, which implies the exothermic nature of adsorption [61]. The thermodynamic parameters were evaluated using Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) are evaluated using equations below [62, 63]:

$$\Delta G^\circ = -RT \ln K_a;$$

$$K_a = \frac{(1000 \cdot \text{molecular weight}) \cdot K_L \cdot [\text{Adsorbate}]}{\text{coefficient of activity}};$$

$$\ln K_a = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

R (8.314 J/mol K) is the constant of gas, K_a is constant without unit also T present the temperature (K). Several studies revealed that the equilibrium constant (K_a) must be dimensionless in order to have accurate results regarding the Gibbs free energy [63]. The negative or positive values of ΔG° indicate the spontaneity (or non-spontaneity) of the adsorption process [64]. The positive values of ΔS° suggests that the organization of the adsorbate at the solid/solution interface becomes more random, while negative value suggests the opposite fact. The positive values of enthalpy change ΔH° proposed that the adsorption process is endothermic, however the negative values of ΔH° suggest that the adsorption is exothermic [65]. The values of ΔH° and ΔS° were recapitulated in Table 4.

Table 1 The equations and constant parameters for the studying models

Model	Parameters
Pseudo-first-order model $q_t = q_e (1 - e^{-k_1 t})$	q_e present the adsorption capacity at equilibrium and q_t at the time, however, k_1 (min^{-1}) is the rate constant of pseudo-first-order model
Pseudo-second-order model $q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	q_e and q_t presents the adsorption capacities at equilibrium and at the time, k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) is the rate constant of pseudo-second-order model
Langmuir model $q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	q_e (mg/g) and C_e (mg/L) are the capacity of adsorption and dye concentration at equilibrium respectively, q_m is the maximum capacity and K_L (L/mg) is constant of Langmuir model
Dubinin–Radushkevich $q_e = q_s \exp(-K_{ad} \varepsilon^2)$	q_e and q_s are the capacity of adsorption at equilibrium and maximum respectively, and K_{ad} is free energy of adsorption per mole of adsorbate (mol^2/J^2) and ε Polanyi potential that is calculated using this equation: $\varepsilon = RT \cdot \ln \left(1 + \left(\frac{1}{C_e} \right) \right)$; where, R is the universal gas constant (8.314 J/mol. K), T is the temperature in Kelvin (K) and E the mean adsorption energy that is calculated using this equation: $E = \frac{1}{\sqrt{2K_{ad}}}$
Freundlich model $q_e = K_F C_e^{\frac{1}{n}}$	$1/n$ present the heterogeneity factor, K_F (mg/g (L.mg)) $^{1/n}$ is the adsorption capacity related to Freundlich isotherm. Values of $n < 1$, $1 < n < 2$ and $2 < n < 10$ show poor, difficult and good adsorption characteristics, respectively

Table 2 The pseudo-first-order kinetics, and the pseudo-second-order kinetics for dyes adsorption onto HAP-CTS-Mt

		IC	MO	MB
Pseudo first-order	q_e Experimental	99.872	96.641	47.914
	q_e calcul (mg/g)	97.553	90.057	46.094
	K_1 (min^{-1})	0.058	0.136	0.049
	R^2	0.95	0.93	0.959
	χ^2	61.436	73.794	11.263
Pseudo second-order	q_e calcul (mg/g)	102.131	99.16	48.551
	K_2 (g/mg min)	6.52×10^{-4}		
	R^2	0.981	0.975	0.989
	χ^2	35.557	25.978	5.634

Fig. 7 Experimental data and the fitted non-linear forms of pseudo-first-order kinetics, and the pseudo-second-order kinetics for dyes adsorption onto HAP-CTS-Mt

Fig. 8 Non linear fitting of the Dubinin–Radushkevich, Langmuir and Freundlich isotherms models for the adsorption of IC, MO and MB using HAP–CTS–Mt thin film

Table 3 Isotherm constants and correlation coefficients for the adsorption of dyes on HAP–CTS–Mt

		IC	MO	MB
Langmuir model	q_m (mg/g)	243.18	137.5	168.52
	K_L (L/mg)	1.21	0.49	0.178
	χ^2	52.6	99.83	124.07
	R^2	0.996	0.98	0.993
Freundlich model	K_F (mg/g (L/mg)) ^(1/n)	110.27	51.69	52.21
	N	5.59	4.63	4.23
	χ^2	1145.51	392.65	716.49
	R^2	0.915	0.883	0.85
Dubinin–Radushkevich	q_s (mg/g)	235.17	132.11	155.77
	χ^2	155.88	96.31	30.42
	K_{ad} (mol ² /J ²)	2.04×10^{-4}	0.00146	0.0043
	E (J/mol)	49.507	18.5	10.78
	R^2	0.988	0.971	0.974

Table 4 Thermodynamic parameters for the adsorption of dyes onto HAP-CTS-Mt

	ΔH° kJ/mol	ΔS° J/mol K	ΔG° kJ/mol				
			293 K	303 K	313 K	323 K	333 K
IC	-54,42	-66,29	-35,40	-34,10	-33,14	-32,95	-32,75
MO	-45,65	-49,76	-31,46	-30,15	-29,88	-29,57	-29,33
MB	-17,83	36,44	-28,48	-29,04	-29,10	-29,61	-30,02

Fig. 9 Reusability study of HAP-CTS-Mt with IC, MO and MB

The ΔG° values indicate that the adsorption of the three dyes using HAP-CTS-Mt was spontaneous and favorable; the rise in ΔG° with increasing temperature indicates that the adsorption is favorable at 293 K. The ΔH negative values (-54.42 kJ/mol K; -45.65 kJ/mol K and -17.83 kJ/mol K for IC, MO, and MB, respectively) confirm the exothermic nature of adsorption [66]. The calculated ΔS° value was found to be negative; this corresponds to a decrease in the degree of freedom of the adsorbed species. However, the ΔS° value of MB dye adsorption onto HAP-CTS-Mt was found to be positive which indicates a slight increase in disorder at the solid-adsorbate interface during adsorption process.

4.8 Regeneration study

The regeneration of the adsorbent is an important step in order to recover the dye and reuse the prepared adsorbent in several cycles of adsorption [67]. After adsorption at optimal conditions regarding each dye the HAP-CTS-Mt/dye was washed several times with distilled water to remove any unadsorbed dyes. Thereafter, the HAP-CTS-Mt/dye was desorbed using 3.0 M NaOH. The regenerated HAP-CTS-Mt was washed with distilled water, dried in open air and reutilized thereafter. The adsorption-desorption of HAP-CTS-Mt for the three dyes was presented in Fig. 9.

It was observed that the removal of dyes was efficient up to 3 cycles for the three studied dyes, which implies that the film can be utilized several times before complete exhaustion.

4.9 Comparison study of the adsorption of IC, MO and MB using different adsorbents

The adsorption capacities of IC, MO and MB onto HAP-CTS-Mt thin film have been compared with those of others reported in the literature as presented in Table 5. It is notice that HAP-CTS-Mt has higher adsorption capacities among other adsorbent such as chitosan, chitosan/activated carbon, chitosane biomass, magnetic chitosane and Alginate-Chitosan-Montmorillonite (Table 5).

Table 5 Maximum loading capacities (Langmuir model) for IC, MO and MB adsorption

Adsorbent	Adsorbate	q (mg/g)	References
Chitosan	IC	71.28	[68]
Chitosan/activated carbon	IC	208.33	[69]
Chitosane biomass	MO	29	[70]
Magnetic chitosan	MB	60.4	[71]
Alginate-Chitosan-Montmorillonite	MB	137.15	[72]
Montmorillonite nanosheets/chitosan	MB	530	[73]
HAP-CTS-Mt	IC	250	Current study
HAP-CTS-Mt	MO	142.86	Current study
HAP-CTS-Mt	MB	166.67	Current study

5 Conclusion

In this work, the HAP–CTS–Mt film was elaborated and characterized by FTIR and XRD. The adsorption of IC, MO, and MB from aqueous solution onto HAP–CTS–Mt was also examined. The results showed that the HAP–CTS–Mt film was able to remove IC, MO, and MB dyes. The adsorption of the three studied dyes using this new film followed the Langmuir isotherm model, with maximum adsorption capacity of 243.18 mg/g, 137.5 mg/g and 168.52 for IC, MO, and MB, respectively. The optimal adsorbent dose for IC and MB was 0.2 g/L, 0.5 g/L for MO. At optimum concentration of 20 mg/L, 50 mg/L and 20 mg/L for IC, MO and MB respectively. The adsorption of IC, MO and MB was fitted by the pseudo-second order model. The adsorption of the three dyes using HAP–CTS–Mt was exothermic and spontaneous. The possible mechanisms for the adsorption of IC, MO and MB using HAP–CTS–Mt thin film were also explained. Moreover, the desorption and regeneration experiments showed excellent adsorption performance even after 3 adsorption–desorption cycles.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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