Covalent organic framework and montmorillonite nanocomposite as advanced adsorbent: synthesis, characterization, and application in simultaneous adsorption of cationic and anionic dyes

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Abstract

In this work, Schiff base network-1 (SNW-1), as a new generation of covalent organic frameworks (COFs), was synthesized and modified by fabrication of a composite with clay mineral montmorillonite (Mt). It was used for simultaneous removal of anionic and cationic dyes from aqueous solutions. The fabricated composite was characterized successfully with various techniques. Tartrazine (TT) and methylene blue (MB) were selected as model anionic and cationic dyes, respectively. The effects of the percentage of each component in the composite, initial pH, and initial dye concentration were evaluated on the adsorption capacity. Adsorption reaction models and adsorption diffusion models were used to study the kinetic process of adsorption. Adsorption of both dyes reached equilibrium after 40 min. The obtained results were fitted to Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) models to predict the isotherms of adsorption. Under optimum conditions for removal of each dye with the composite, the maximum adsorption capacity of 519.2 and 602.7 mg g⁻¹ were obtained for TT and MB, respectively. The used SNW-1/Mt composite could be regenerated by salty methanol. The high adsorption capacity and excellent reusability make SNW-1/Mt composite attractive for the simultaneous removal of anionic and cationic dyes from aqueous solutions.

Keywords Covalent organic framework · Montmorillonite · Simultaneous removal · Tartrazine · Methylene blue · Water treatment

Introduction

Wastewater containing dyes discharging from factories producing plastic, paper, food, textiles, and cosmetics is an important source of environmental pollution [8, 39]. Almost 7×10^5 tons of dyes are produced yearly, and about 30% of the world's total production of dyes may be lost during their consumption [62]. The dye-containing wastewater is hazardous to fish and other organisms and affects natural aquatic systems by adsorbing sunshine and resisting photosynthesis [19]. Due to their high molecular mass and complex structure, organic

dyes are usually difficult to degrade. Non-biodegradable dyes can affect human health by inducing mutagenesis and carcinogenesis illnesses [62]. Dyes have several types: anionic (acidic) and cationic (basic) dyes are two important groups of water soluble synthetic dyes. Tartrazine (TT) is an anionic dye widely used in food products, pharmaceuticals, cosmetics, drugs, and textile fibers [41]. TT can cause asthma, migraines, eczema, thyroid cancer, and behavioral problems in humans by causing hyperactivity [38]. Methylene blue (MB), as the most common stain, is a water soluble cationic dye and has a significant impact on human health due to toxicity and causes carcinogenic, mutagenic, or teratogenic effects [36].

Different methods for removal of dyes have been reported, including adsorption [39, 40], coagulation and flocculation [47], oxidation [48], and membrane separation [6]. The adsorption method is simple and also popular due to its high capacity, high speed, high efficiency, low cost, applicability to large-scale, and ability to regenerate active surface of adsorbents [23]. In addition, pigments can be produced by adsorption of dyes on inorganic supports such as silica [30, 31]. Many adsorbent materials have been introduced for removal

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of TT, such as activated carbon of Lantana [16], chitin [10], and amberlite [55]. Moreover, some adsorbents have been introduced for removal of MB, such as biosynthesize copper oxide nanoparticles [50], Kaolin [42], and carbon nanotubes (CNTs) [59]. The features of adsorbents are the main parameters for their selection from the diverse range of adsorbents used for removal. Therefore, selection of cheap adsorbents with high adsorption capacity is very important.

Nanoporous frameworks are divided into metal organic frameworks (MOFs) and porous organic frameworks (POFs). MOFs [63] are the first family of hybrid materials in which metal ions are linked together by organic bridging ligands. Generally, MOFs have tunable pore sizes and high apparent specific surface areas, and can selectively uptake small molecules. Low physical and chemical stability (e.g. collapse under hydrothermal conditions or in water/acidic/basic solutions) is their limitation. POFs have five sub-groups the features of which are close to each other with infinitesimal differences. Porous aromatic frameworks (PAFs) [3], polymers of intrinsic microporosity (PIMs) [4], conjugated microporous polymers (CMPs) [21], hyper-cross-linked polymers (HCPs) [57], and covalent organic framework (COFs) [7, 13] are parts of POFs hybrid materials. Among them, COFs have gained attention due to their inherent porosity, well-defined pore aperture, ordered channel structure, large specific surface area, high stability, and multi-dimensionality. Recently, COFs were employed for removal and adsorption of dyes from aqueous samples [1, 46, 53]. In addition to the fabulous features of COFs, raw materials of most of these adsorbents are too expensive and require catalysts for synthesizing. Schwab et al. [49] introduced low-cost catalyst-free melamine-based polymer networks through Schiff base chemistry for synthesizing nitrogen-rich series of Schiff base networks (SNWs). Among these series, SNW-1 with a high specific surface area was synthesized through polymerization of melamine and terephthalaldehyde in dimethyl sulfoxide (DMSO) solvent, which is cheap and reachable. Generally, fabrication of POFs is pricey which needs expensive raw material such as boron-containing materials and their derivatives [7, 27], specific reactor apparatus such as sealed Pyrex tube [7] and microwave [56], and high price catalysts such as palladium [32]. SNW-1 has catalyst free synthetic procedure that melamine and terephthalaldehyde as its cheap and accessible raw materials, react under simple reflux condition.

Montmorillonite (Mt) is a kind of natural 2:1 type layered clay mineral with high cation exchange capacity, high specific surface area, and swelling ability. Mt with the chemical formula of $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$ is composed of units made of two silica tetrahedral sheets with a central aluminum octahedral sheet, and water and cations between its layers neutralize its negative charge. As a cheap and readily available mineral with many excellent properties, Mt has been widely used in a number of research industrial

branches [5, 60]. Due to its cation exchange capacity, small particle size, bearing constant negative charge on its surface, and sheet-like structure, Mt may be particularly suitable to be used as an adsorbent for removal of cationic dyes. Recently, composites of Mt were used as effective adsorbent for removal of dyes [51, 54].

Most adsorbents have applicability to remove either cationic or anionic dyes [25]. Simultaneous removal of cationic and anionic dyes is challenging. Primary experiments showed that SNW-1 and Mt have opposite charge surfaces and that they have high tendency for adsorption of anionic and cationic dyes, respectively. Therefore, a nanocomposite was fabricated by grounding positive SNW-1 on the surface of Mt layers for simultaneous removal of TT and MB as model anionic and cationic analytes from aqueous solutions. The effect of the composition of the composite, initial pH of the solution, and initial concentration of dyes on the removal efficiency of the dyes were studied. The kinetic process and isotherm models of adsorption were evaluated. Finally, the applicability of the fabricated composite for regeneration and removal of dyes from environmental water samples was examined.

Experimental

Chemicals and materials

All chemicals were of analytical-reagent grade. TT, MB, Mt powder, and terephthalaldehyde were purchased from Sigma-Aldrich (Milwaukee, WI, USA). 2,4,6-Triamino-1,3,5-triazine (melamine) was obtained from Merck (Darmstadt, Germany). The ultrapure water consumed was purified on a Youngling ultrapure water purification system (model: Aqua MaxTM-ultra) (Seoul, South Korea). Other chemicals such as anhydrous DMSO, sodium hydroxide (NaOH), hydrochloric acid (HCl), methanol (MeOH), ethanol (EtOH), acetone, acetonitrile (ACN), tetrahydrofuran (THF), dichloromethane, and sodium chloride (NaCl) were of analytical reagent grade or of the highest purity available.

Preparation of SNW-1

The SNW-1 nanoparticles were prepared by a solvothermal method which was introduced in a previous study [49]. Shortly, melamine (2.423 g) and terephthalaldehyde (3.870 g) were dissolved in 120 mL of anhydrous DMSO and transferred into a 200 mL single-necked flask. The mixture of these materials was agitated (700 rpm) with a magnetic stirrer bar hot plate and refluxed for 72 h under the protection of Ar gas. The temperature of the reaction was kept constant at 180 °C by a silicon oil bath. After a day, the resultant white to yellow precipitate was observed, but the reaction was continued up to 3 days to complete polymerization. At the end of the

reaction, the hot plate was turned off and the mixture was held under reflux in the silicon oil bath to decrease its temperature down to the room temperature. Finally, the resultant mixture was centrifuged at 4000 rpm for 10 min and the precipitate was washed several times with acetone, dichloromethane, THF, and MeOH in sequence, and then it was dried at 70 °C overnight.

Preparation of Mt/SNW-1 composite

Mt and SNW-1 have opposite surface charges at neutral pH. In addition to electrostatic interactions, due to the existence of hydroxyl groups on the surface of Mt and amine groups in SNW-1, Mt layers can make hydrogen bond interactions with SNW-1 nanoparticles. 2 g of Mt and SNW-1 were dispersed separately in 500 mL distilled water with an ultrasonic bath and magnetic stirrer bar for 15 min, respectively. Then, the Mt solution was added dropwise to the SNW-1 solution. By neutralization of charges, the speed of precipitation increased. After precipitation, the supernatant solution was drawn and the precipitate was dried at 80 °C for 12 h.

Characterization techniques

Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM), energy-dispersive X-ray (EDX), nitrogen gas adsorption for measuring specific surface areas, and zeta potential were used to characterize the surface of the adsorbents. For more details, please refer to Supporting information section.

Removal experiment

The removal efficiency of TT and MB were studied through batch method by dispersing 10 mg of the composite in 20 mL of the dye solutions. Firstly, 10,000 mg L⁻¹ of a stock solution of the dyes were prepared and stored in a dark place at room temperature. The diluted working solutions were prepared from the stock solution. Parameters were optimized using 20 mL of 20 mg L⁻¹ of the dyes at room temperature, and the mixture was stirred on a magnetic stirrer (1000 rpm) in a dark place. After 60 min, the composite was separated from the solution by centrifugation at 4000 rpm for 10 min, and the supernatant solution was transferred to a quartz cell and determined by a UV-Vis instrument (model: Cecil CE7200, 7000 Series) at 426 and 291 nm for TT and MB, respectively. The adsorption capacity (q_t), the distribution coefficient (K_d), and the removal efficiency ($R\%$) of TT and MB in the removal process were calculated using Eqs. 1–3:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

$$K_d = \frac{(C_0 - C_e)V}{C_e \times m} \times 1000 \quad (2)$$

$$R\% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (3)$$

In these equations, C_0 and C_t (mg L⁻¹) are the initial dye concentration and the dye concentration at time t (min). V (L) and m (g) are the volume of the solution and the mass of the adsorbent, respectively, and C_e (mg L⁻¹) is the equilibrium dye concentration after the removal process.

Results and discussion

Characterization of SNW-1 and Mt/SNW-1 nanocomposites

FT-IR measurements

FT-IR measurements were applied to evaluate the functional groups of the synthesized materials. Fig. S1 shows the FT-IR spectra of melamine, terephthalaldehyde, and SNW-1. Bands at 3472, 3421 (NH₂ stretching) and 1651 cm⁻¹ (NH₂ deformation) can be ascribed to the primary amine group of melamine as well as to the carbonyl group of aldehydes at 2866 (C-H stretching) and 1693 cm⁻¹ (C=O stretching), which are strongly attenuated or absent in the spectra of SNW-1, confirming that SNW-1 was synthesized correctly. The FTIR spectrum which was shown in Fig. 1a, the Mt clay has characteristic peaks at 3626, 3427, 1636, 1045 and 525 cm⁻¹ which can be attributed to stretching vibrations of –OH group, stretching vibrations of water associated with the clay, free surface hydroxyl groups on the Mt, stretching of Si-O, and stretching of Si-O-Al bonds, respectively [20, 52]. During the nanocomposite production procedure, these bonds may be swapped by hydrogen bonding interaction [52]. The characteristic peak of stretching vibrations of –OH group of Mt at 3626 was shifted to 3617 due to hydrogen bonding interaction by formation of the composite. The FT-IR spectra of SNW-1, Mt, and the 50:50 (w/w) composite of SNW-1 and Mt are shown in Fig. 1a. All peaks of SNW-1 and Mt are observed in the composite spectrum. These results show that Mt and SNW-1 can make various interactions such as hydrogen bonding, π - π , and Van der Waals interactions with analytes.

XRD measurements

XRD is a unique technique in determination of the structure and crystallinity of materials. There are two different major types of nanocomposite fabrication with clays: intercalated and exfoliated. Intercalated nanocomposites hold interlayer arrangement but their intergallery spacing is amplified or decreased. Due to intercalating, basal spacing diffraction peak usually shifts to

Fig. 1 a FT-IR spectrums and (b) XRD patterns of Mt, the composite, and SNW-1

lower angles. If intercalating agents have large size, distance between layers increase too much that causes spread of layers into different directions. Due to this spread, basal spacing diffraction peak of the clay eliminates or its intensity decreases significantly in exfoliated nanocomposites [33]. The XRD patterns of Mt, SNW-1, and the composite are presented in Fig. 1b. SNW-1 does not have specific peaks due to its amorphous structure, and there is just a peak near 20°, which is broad due to the small size of SNW-1 nanoparticles. Mt has a crystalline structure, and its peaks can be seen in the XRD pattern of the composite. Due to the exfoliation of regular stacking layers of Mt nanosheets in the nanocomposite, reduction of peak intensity was happened. As shown in Fig. 1b, Mt clay has diffraction peaks at $2\theta = 19.7^\circ$, 26.5° , and 34.9° which are well matched to the previously reported studies [9, 14]. In a reported study [9], Mt has a strong basal spacing diffraction peak $d(100)$ at $2\theta = 5.87^\circ$ which reduced significantly and a broad weak peak appeared at $2\theta = 5.68^\circ$ after fabrication nanocomposite with TiO₂ particles. According to low angle XRD pattern of the fabricated SNW-1/Mt composite (Fig. S2), there is a broad weak peak at $2\theta = 5.61^\circ$ which shows the layers Mt clays exfoliated and spread in different directions.

FE-SEM, TEM, and EDX measurements

The structure, size, morphology, and composition of the fabricated hybrid were characterized by SEM, TEM, and EDX. The SEM images of pure Mt clay are shown in Fig. S3, which display Mt clay has stacking 2D layers. The SEM images of SNW-1 nanocomposite are displayed in Fig. 2a and b. This nano-material has particle sizes between 40 and 60 nm. As shown in Fig. 2e and f, SNW-1 nanoparticles were attached on both surfaces of Mt layers and produced a three-dimensional nanostructure hybrid material. This indicates that the assembly of SNW-1 on the Mt surface was successfully obtained. The TEM image of the composite confirms the results obtained with SEM. The TEM images of SNW-1 are displayed in Fig. 2c and d. The TEM images of the composite are shown in Fig. 2g and h. As shown in the TEM images, SNW-1 nanoparticles have spherical structure, Mt has layer structure, and in the composite, the layers of Mt passed through SNW-1 nanoparticles. The EDX spectrum of Mt in Fig. 3a shows Mg, Ca, K, and Na cationic elements which neutralize the negative layers of Mt. These cations disappeared in the EDX of the composite (Fig. 3b) and just the elements of SNW-1 and the layers of Mt can be seen. The negative layers of Mt need opposite charge materials to prevent the destruction of its structure. Therefore, observations show that SNW-1 diffused into the layers of Mt and by exfoliation stacking layers of Mt clay, SNW-1 nanoparticles were replaced with other cations. In the EDX spectrum of the composite, C, N, O, Si, and Al have the highest percentages in the composition, which confirms that both SNW-1 and Mt had portion in the skeleton of the composite.

Nitrogen adsorption and desorption measurements

The results obtained from the typical nitrogen adsorption-desorption isotherms and the pore size distribution curves of Mt, SNW-1, and the composite are shown in Fig. 4. For Mt, the isotherm shows the type III shape (according to Brunauer-Deming-Deming-Teller (BDDT) classification system) with hysteresis type H4 loops (according to IUPAC classification) indicating the presence of mesopores in Mt. The isotherm of SNW-1 and the composite shows the type II shape with hysteresis type H4 loops. As previously reported in the synthesis of SNW-1 [61], this hysteresis loop was observed upon desorption, revealing the microporous framework with mesopores formed by close-packed nanoparticles.

In previous articles [45, 49, 61], the reported specific surface areas of SNW-1 vary from 133 to 1377 m² g⁻¹. This was probably obtained from differences of particle sizes, degrees of cross-linking, and open channels produced under different synthetic conditions. Another important issue that may have an effect on the specific surface area is the existence of DMSO in the pores of SNW-1 remaining from the synthesizing process. DMSO can be replaced with low boiling solvents such as MeOH by washing

Fig. 2 FE-SEM images of SNW-1 (a and b), TEM images of SNW-1 (c and d), FE-SEM images of the composite (e and f), and TEM images of the composite (g and h)

the resulted adsorbent and activation under thermal conditions in the oven. By increasing times of washing, the replacment of

DMSO will increase, and the adsorbent will show a higher specific surface area. In the present work, the adsorbent was

Fig. 3 EDX spectrums of (a) Mt, and (b) the composite

Fig. 4 (a) The N_2 adsorption/desorption isotherms and (b) pore size distributions of SNW-1, Mt, and the composite

dispersed in aqueous media. Therefore, high order exchange of DMSO and activation of SNW-1 is not necessary. However, activation is important in gas/solid interface extraction.

According to the isotherms of BET, SNW-1, Mt, and the composite, all of them have large specific surface areas of 201.6, 58.1, and 183.3 m² g⁻¹, respectively. Furthermore, as shown in Fig. 4b, the BJH adsorption pore size distributions of Mt, SNW-1, and the composite, respectively. The adsorbents with the pore size smaller than 2 nm, between 2 and 50 nm, and higher than 50 nm are classified as microporous, mesoporous, and macroporous adsorbents, respectively. SNW-1 and Mt have micropore and mesopore distribution. The composite shows micropore and mesopore distribution due to the existence of SNW-1, Mt, and a broad macroporous distribution which continued up to 100 nm. This broad macroporous distribution can be seen in the composite, which did not appear in Mt and SNW-1. This may be due to exfoliation the layers of Mt clay with SNW-1 nanoparticles. Due to exfoliation of Mt layers, hysteresis loop of the N₂ adsorption/desorption of the composite became wider and its average pore size increased which are well matched with previously reported study [9].

Zeta potential distribution measurements

Zeta potential distributions were analyzed in the distilled water solution (pH ~ 6). The data are shown in Fig. S4. According to Fig. S4a and b, SNW-1 and Mt have positive and negative zeta potentials, respectively. These results show that SNW-1 and Mt can make electrostatic interactions with anionic and cationic analytes, respectively. According to Fig. S4c, the composite has a broad distribution of surface charges from negative to positive, which confirms that the composite is a good adsorbent to make electrostatic interactions with both cationic and anionic analytes.

Effect of the composition of the composite on dye removal

The removal of dyes by SNW-1, Mt, and the composite from the aqueous solution was investigated. The comparison between the adsorbents toward the dye adsorption can be expressed by determination of q_t . Removal experiments with the individual solutions of TT and MB were performed, and q_t values were calculated. SNW-1 is a multifunctional adsorbent with a positive surface charge. It can make hydrogen bonding, π - π interactions, and Van der Waals interactions with analytes. According to Fig. 5a and b, pure SNW-1 adsorbed both TT and MB, but due to the positive surface charge, it had a high tendency to TT as anionic dyes. Mt has a negative layer in its structure, and it is a good candidate for removal of cationic dyes. There are silanol groups on the surface of Mt layers which can interact by hydrogen bonding and electrostatic interactions with analytes. Due to its negative charge, Mt can adsorb MB on

the surface of its layers. Therefore, for the simultaneous removal of anionic and cationic dyes, a composite of SNW-1 and Mt can be a suitable adsorbent for both dyes. Different hybrid materials with various percentages of SNW-1 and Mt (w/w) were prepared, and their efficiency toward removal of individual TT and MB were investigated by determination of q_t . According to the results, by increasing the percentage of Mt in the composition of the hybrid material, the amount of MB adsorption increased, and in contrast, the amount of TT adsorption decreased. The produced hybrid material with equal percentage of each component was the optimized adsorbent for simultaneous removal of TT and MB.

Effect of pH on dye removal

In the process of dye removal, the pH of the solution, due to its influence on ionization of the functional groups of the adsorbent, is a key factor. Salt usually has a negative effect on the efficiency of nanoporous frameworks [58]. To eliminate the effect of salt, two batches contain 20 mL of 20 mg L⁻¹ of un-buffered individual dyes were prepared, and their pHs were adjusted by dropwise addition of the dilute HCl or NaOH solutions. According to Fig. 5c, the adsorption capacity of TT decreased by increasing the pH. In aqueous media, TT was first dissolved and the sulphonate groups of TT (X-SO₃Na) were dissociated and converted to anionic dye ions (X-SO₃Na $\rightleftharpoons$ X-SO₃⁻ + Na⁺). At low pHs, the composite had more positively charged sites due to protonation of the functional groups. Moreover, the silanol groups were neutral at low pHs, and in addition to an increase in hydrogen bonding, the electrostatic repulsion with the anionic sulphonic groups of TT dye molecules decreased. On the other hand, the number of protonated functional groups decreased at higher pHs and more OH⁻ anions were available to compete (repulsion effect) with the anionic sulphonic groups of TT dye molecules [16]. Therefore, the adsorption capacity for TT molecules decreased at higher pHs.

In contrast, as shown in Fig. 5d, the adsorbed MB dye molecules increased by increasing the pH, similar to previously reported results [11]. This might be due to the high concentration of negative charges of the adsorbent at high pH values.

When the pH of the adsorption system rose, due to deprotonating of the silanol groups, the number of negatively charged sites on the surface of the composite increased [16]. Due to the presence of excess H⁺ ions that competed with MB for the adsorption sites at lower pH values, adsorption of MB molecules decreased.

Kinetic process of adsorption

To this day, different mathematical models have been introduced to describe adsorption data. Generally, these models can be classified as adsorption reaction models and adsorption diffusion models. Although both models are applied to describe the kinetic process of adsorption, they are quite different in nature.

Fig. 5 Effect of the composition of the composite and initial pH of the solution on removal of TT (a and c) and MB (b and d) from the aqueous solution (Experiment conditions: 20 mL of 20 mg L^{-1} colored solution, 10 mg adsorbent, 60 min extraction, 1000 rpm stirring)

Adsorption diffusion models have three consecutive steps [35]: (1) diffusion across the liquid film surrounding the adsorbent particles (external diffusion or film diffusion); (2) diffusion in the liquid contained in the pores and/or along the pore walls (internal diffusion or intra-particle diffusion); and (3) adsorption and desorption between the adsorbate and active sites (mass action or chemisorption). However, adsorption reaction models, which consist of pseudo-first-order and pseudo-second-order models, are based on the whole process of adsorption without considering these steps mentioned above. An introduction to adsorption reaction and diffusion models can be found in Supporting information section.

The kinetic adsorption of dyes was studied in aqueous solutions containing the composite (50–50% (w/w) Mt/SNW-1) in order to understand the kinetic mechanism of the composite and adsorption reaction and diffusion models. Figure 6a and b show the effects of contact time on the adsorption of TT and MB with the composite, respectively. In the following sections, these results are discussed thoroughly.

Adsorption reaction models

According to Fig. 6a and b, as contact time increased, saturation of sites increased until the adsorption equilibrium was

reached within 40 min. The experimental data obtained were fitted to the Lagergren's first order kinetic (Eq. S1) and the Ho's pseudo-second-order (Eq. S2) models to evaluate the adsorption kinetics of TR and MB on the composite [29, 34]. According to different adsorption reaction models, the corresponding model parameters were calculated through the slope and intercept of the respective fitted straight line, which are shown in Fig. S5 and are summarized in Table 1.

By comparing the values of correlation of determination (R^2), the pseudo-second-order model (1.0 and 0.9999 for TT and MB, respectively) is more suitable than the pseudo-first-order kinetic model (0.8088 and 0.7556 for TT and MB, respectively) to describe the TT and MB adsorption kinetic behavior on the composite. These results show that the chemical adsorption process is a kinetic limiting step. In addition, the $q_{e,cal}$ values, as obtained from the pseudo-second-order kinetic model, are very close to the experimentally observed values (q_{exp}).

Adsorption diffusion models

Both adsorption reaction models and adsorption diffusion models are widely employed for fitting kinetic data. Generally, adsorption reaction models cannot represent the real process of adsorption and thus cannot provide useful

Fig. 6 Effects of contact time on adsorption of (a) TT and (b) MB with the composite; and effects of the initial concentration of (c) TT and (d) MB on adsorption capacity (Experiment conditions: 20 mL of 20 mg L⁻¹ colored solution, 10 mg adsorbent, pH = 6, 1000 rpm stirring)

information to gain insight into the adsorption mechanism. However, adsorption diffusion models can give a brighter insight into the adsorption mechanism with more details.

To establish the diffusion mechanism of dyes (20 mg L⁻¹ of each dye) into the composite, two commonly used models for adsorption rate-controlling step, i.e. the intra-particle diffusion model (Eq. S3) and film diffusion model (Eq. S4) [44], were employed. According to different adsorption diffusion models, the corresponding model parameters were calculated through the slope and intercept of the respective fitted straight line, which are shown in Fig. S6 and are summarized in Table 2. The R^2 s (from 0.9115 to 0.9814) of the fitting straight lines from the film diffusion model were higher than the R^2 s (from 0.7231 to 0.7537) of the intra-particle diffusion model.

The above analyses implied that film diffusion has a greater effect on the adsorption rate-controlling step than intra-particle diffusion. Intra-particle diffusion and chemisorption through chemical bonding might be present in the adsorption rate-controlling steps.

Adsorption isotherm models

The adsorption isotherm is an effective tool to study the adsorption mechanism of an adsorption process. Important results such as the adsorption nature of the removal process and the adsorption capacity of the adsorbent can be obtained from isotherm models.

Table 1 Adsorption reaction parameters for removal of TT and MB on the composite

		Pseudo-second order			Pseudo-first order		
		$t/q_t = \frac{1}{(K_2 q_e^2)} + \left(\frac{1}{q_e}\right)t$			$\log(q_e - q_t) = \log q_e - (K_1/2.303)t$		
Dye	q_{exp}	$q_{e, cal}$ (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	R^2	$q_{e, cal}$ (mg g ⁻¹)	k_1 (1 min ⁻¹)	R^2
TT	32.16	32.47	0.037	1	6.44	0.009	0.8088
MB	39.88	40.32	0.026	0.9999	5.70	0.052	0.7556
		V = 20 mL	m = 10 mg	V/m = 2000	$C_0 = 20$ mg L ⁻¹		

Table 2 Adsorption diffusion parameters for removal of TT and MB on the composite

	Intra-particle diffusion model			Film diffusion model	
	$q_t = k_{id}t^{0.5} + C$			$\ln(1-F) = k_f t^* F = \frac{q_t}{q_\infty}$	
Dye	$k_{id} \text{ (mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2})$	C	R^2	$k_f \text{ (min}^{-1})$	R^2
TT	0.669	26.351	0.7231	0.073	0.9814
MB	1.146	31.551	0.7537	0.059	0.9115
	V = 20 mL	m = 10 mg	V/m = 2000	$C_0 = 20 \text{ mg L}^{-1}$	

Figure 6c and d show the effects of the initial concentration of TT and MB on the adsorption capacity, respectively. Adsorptions took place in the distilled water (pH = 6) at room temperature for 12 h to assure adsorptions were completed. The equilibrium data were analyzed by Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherm models. Their equations are shown as Eqs. S5–10. The adsorption isotherm models can be found in Supporting information section. According to different adsorption isotherm models of TT and MB with the composite, the corresponding model parameters were calculated through the slope and intercept of the respective fitted straight line, which are shown in Fig. S7 and S8, respectively. The isotherm model constants and the calculated coefficients are summarized in Table 3.

According to IUPAC classification of adsorption isotherms, the TT removal in Fig. 6c is demonstrated as the second class with a break point. The results show the adsorption process of TT from monolayer to multilayer adsorption, and the breakpoint meant the end of the monolayer adsorption, and simultaneously, the beginning of the multilayer adsorption [2]. Thus, according to Fig. 6d, by increasing the concentration of MB, the adsorption capacity of MB on the

composite increased and then leveled off. This pattern shows that the adsorption of MB on the composite is monolayer.

According to Table 3, results show that the R^2 obtained from the Freundlich isotherm model is the highest for removal of TT. Additionally, the R^2 obtained from the Langmuir is the highest for removal of MB by the composite. Therefore, the adsorption of TT on the composite is multi-layer and the adsorption of MB on the composite is monolayer.

Reusability study

To evaluate the possibility of regeneration and reusability of the composite, the desorption experiments were evaluated. The desorption of dyes, and thus the regeneration of the composite, was divided into three parts. In the first experiment, the desorption and regeneration of the composite were achieved using pure MeOH, EtOH, DMSO, THF, acidic water (1 M HCl), basic water (1 M NaOH), ACN, and acetone. The desorption efficiency for DMSO was the highest, and for acidic and basic water, it was moderate, and it was poor for other solvents. For the second experiment, NaCl salt, as the source of cation and anion, was added to each of the solvents and its

Table 3 Adsorption isotherm parameters for adsorption of dyes onto the composite

Isotherms	Parameters	Dyes	
		TT	MB
Langmuir model $\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{b q_m}$	$q_m \text{ (mg g}^{-1})$	74.627	75.758
	$b \text{ (L mg}^{-1})$	0.064	0.846
	R^2	0.9948	0.9999
Freundlich model $\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	$K_F \text{ ((mg g}^{-1}) \text{ (L mg}^{-1})^{1/n})$	24.756	51.707
	n	5.118	13.812
	R^2	0.9985	0.8924
Temkin model $q_e = B \ln A + B \ln C_e$	A	5.898	4820.427×10^2
	$B \text{ (L mg}^{-1})$	9.666	4.104
	R^2	0.9893	0.9020
D-R model $\ln q_e = \ln q_m + B_1 \varepsilon^2$ $\varepsilon = RT \left(1 + \frac{1}{C_e} \right) \ln E = 1 / \sqrt{2B_1}$	$q_m \text{ (mg g}^{-1})$	213.086	72.857
	$B_1 \text{ (mol}^2 \text{ kJ}^{-2})$	0.208	0.001
	$E \text{ (kJ mol}^{-1})$	1.551	31.623
	R^2	0.8030	0.9049

Fig. 7 Adsorption capacity of the composite toward (a) TT and (b) MB after regeneration (Experiment conditions: 20 mL of 20 mg L⁻¹ colored solution, 10 mg adsorbent, pH = 6, 60 min extraction, 1000 rpm stirring)

effect was studied. Evidences showed that DMSO and methanol containing NaCl had the highest desorption efficiency. Sodium cations can reach the surface of the composite, diffuse into the composite, and act as a cation exchanger. Sodium cations can replace with MB cations, which were adsorbed on the surface or between the layers of the composite. On the other hand, chloride anions can replace with anionic TT, which was adsorbed on the surface of the composite. For the third experiment, the effect of the eluent temperature on desorption was evaluated, but no significant effect on desorption was observed. Methanol was preferred due to its lower boiling point in comparison with DMSO. Therefore, the composite was desorbed with saturated salty methanol. After desorption, the composite was washed with distilled water to remove excess salt from its surface or its pores and was dried in the oven before the next use.

The effect of five consecutive adsorption–desorption cycles on removal efficiency was studied, and the results are shown in Fig. 7. The results showed that the adsorption capacity of the dyes on the composite decreased by increasing

Table 5 Comparison of maximum dye adsorption capacity of some adsorbents reported in the literature for removal of TT and MB

Adsorbent	Maximum dye adsorption (mg g ⁻¹)	References
TT		
Activated carbon of <i>Lantana camara</i>	90.90	[16]
Chitosan	350	[10]
Activated carbon of Alligator weed	183.4	[17]
Cross-linked chitosan coated bentonite	294.1	[43]
Amberlite IRA-900	49.88	[55]
Copper coordinated dithiooxamide metal organic framework	320.8	[18]
SNW-1/Mt	519.2	This work
MB		
Teak wood bark	914.6	[37]
Bamboo-based active carbon	454.2	[26]
Filtrisorb 400	476	[12]
Peat	323.7	[15]
Activated sludge biomass	256.4	[22]
Graphene-Fe ₃ O ₄ composite	190.1	[28]
CNTs	46.2	[59]
Clay	6.3	[24]
SNW-1/Mt	602.7	This work

the number of the cycles. These results show that the composite can be regenerated for dye adsorption.

Comparison

Kinetic and isotherm models were studied in distilled water (pH ~ 6). To examine maximum dye adsorption capacity, two individual experiments were done under optimum conditions. For extraction of dyes, 10 mL of 1500 mg L⁻¹ of TT and MB were prepared separately, and the pH of the solutions were set at 3 and 10, respectively. 10 mg of the composite was dispersed to each solution and stirred on the magnetic stirrer overnight (~12 h). After centrifuging, the maximum dye adsorption capacity values of TT and MB were determined (shown in Table 4). The fabricated composite, in addition to its ability to simultaneously remove anionic and cationic dyes, has dye adsorption capacity higher or comparable with other

Table 4 Maximum adsorption capacity of the composite toward TT and MB

Adsorbent	Dyes	C_0 (mg L ⁻¹)	C_f -12 h (mg L ⁻¹)	Maximum dye adsorption (mg g ⁻¹)	K_d (mL g ⁻¹)
SNW-1/Mt	TT	1500	980.8	519.2	529.4
	MB	1500	897.3	602.7	671.7
V = 10 mL	m = 10 mg	V/m = 1000 mL g ⁻¹	Time = 12 h		

Table 6 Removal of dyes with the composite from the river water sample

Adsorbent	Dyes	C_0 (mg L ⁻¹)	C_f 40 min (mg L ⁻¹)	q_t (mg g ⁻¹)	Removal %	K_d (mL g ⁻¹)
SNW-1/Mt	TT	10	0.67	9.33	93.33	13,996
	MB	10	0.57	9.43	94.25	16,382
V = 10 mL m = 10 mg			V/m = 1000 mL g ⁻¹	Time = 40 min		

adsorbents (Table 5), which most of these adsorbents can just remove anionic or cationic dyes. The nanocomposite was produced from cheap raw materials through an easy production procedure. In addition to its high capacity for adsorption of dyes, the fabricated nanocomposite can remove anionic and cationic dyes simultaneously.

Practical application

To demonstrate the applicability of the fabricated composite, a river water sample was collected from Jajrood River (Tehran, Iran). The sample was filtered to eliminate suspended particles. Ten milliliters of the sample was spiked with 10 mg L⁻¹ of TT and MB. Ten milligrams of the adsorbent was dispersed in the colored sample and stirred vigorously on the magnetic stirrer for 40 min. After centrifugation, the residual water was analyzed. The amount of adsorption capacity, percentage of removal, and distribution coefficient were determined (as reported in Table 6). Mixing the yellow TT dye with the blue MB dye resulted in a green mixture, which the colored river sample got transparent after adsorption with the composite. As shown in Fig. 8, TT has $\lambda_{\max}$ at 426 nm and MB has two $\lambda_{\max}$ at 291 and 66 nm which were eliminated or significantly attenuated after removal with the composite adsorbent. The results demonstrated that the fabricated composite was applicable for simultaneous extraction and removal of TT and MB in environmental water samples.

Fig. 8 UV-Vis spectra of mixture 10 mg mL⁻¹ standard solution of TT and MB (a) before and (b) after removal with the composite for 40 min

Conclusions

The composite of SNW-1 and Mt was synthesized, characterized, and successfully applied for simultaneous removal of anionic TT and cationic MB dyes from environmental water samples. The composition of the composite and the initial pH of the solution had an effect on removal efficiency. Kinetic and isotherm models of the adsorption process were studied. Based on the pseudo-second order model, adsorption of TT and MB on the composite is chemisorption. Thus, adsorption diffusion of TT and MB follows the film diffusion model, but that is not the only factor and other factors simultaneously control the adsorption rate. Due to the multi-layer process of the adsorption of TT on the composite, it is better described by Freundlich isotherm model, and in contrast, adsorption process of MB on the composite follows Langmuir isotherm model and it shows that this adsorption is monolayer. The produced composite can regenerate with salty methanol, and due to its high adsorption capacity, it is a good candidate for simultaneous removal of TT and MB from water samples.

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Compliance with ethical standards

Conflict of interest There are no conflicts of interest to declare.

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