Highly ordered pure and indium-incorporated MCM-41 mesoporous adsorbents: synthesis, characterization and evaluation for dye removal

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ABSTRACT

Highly ordered pure MCM-41 and In-MCM-41 mesoporous adsorbents (with Si/In = 95 (IM0.05) and Si/In = 90 (IM0.1)) were synthesized using the hydrothermal-assisted method. The structural, morphological and texture characteristics were investigated by XRD, N₂ adsorption–desorption, SEM-EDX, TEM, diffuse reflectance (DR) and FTIR. The broadening XRD diffraction peaks as well as the shifts to higher and lower 2-theta in IM0.05 and IM0.1, respectively, confirmed the incorporation of indium atoms in the MCM-41 structure. SEM-EDX and TEM images showed that pure MCM-41 and IM0.05 preserve a highly long-range well-ordered hexagonal pore structure, on the other hand, high loading of indium (IM0.1) resulted in partially irregular pore-ordering and morphological defects related to a partial dissolution of MCM-41 structure. The infrared spectra of In-incorporated samples showed a decrease in the transmittance intensity of MCM-41 characteristic peaks with little shifts relative to the pure MCM-41 sample. The potential of pure MCM-41 and In-MCM-41 samples for adsorption of dyes was preliminarily investigated. The removal efficiency of both methylene blue and basic yellow-28 (BY28) was enhanced by the incorporation of indium in the MCM-41. The adsorption equilibrium data of BY28 dye on pure, IM0.05 and IM0.1 samples fitted well with Langmuir adsorption model with adsorption capacity of 123.46, 156.99 and 158.48 mg g⁻¹ respectively. The calculated free adsorption energy obtained from D–R isotherm was found to be 26.7 kJ mol⁻¹ referring to that the adsorption of BY28 on IM0.05 adsorbent is chemical. The adsorption kinetic of BY28 on IM0.05 sample followed the pseudo-second-order model. The adsorption experiments revealed

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that the prepared samples can be used as effective adsorbents for the removal of dyes in aqueous solutions with good recovery and recyclability.

GRAPHICAL ABSTRACT

Introduction

Several tons of commercial dye wastewaters are produced annually by a wide variety of industrial sources, such as printing, textiles and food processing [1–3]. The release of such materials generates unpleasant colored water as the existence of less than 1 ppm of these dyes in water is highly perceptible. Further, discharge of these dyes carries serious threats to living organisms as several dyes and their degradation products are toxic and could be even carcinogenic [4, 5]. Therefore, a growing global concern to treat and remove such hazardous has been conducted. Various chemical, biological and physical techniques such as coagulation, flocculation, membrane separation and adsorption have been progressively investigated to remove color and hazardous materials from contaminated water [6–11]. The physical adsorption technique is one of the most effective routes for dyes removal and controlling of the biochemical oxygen demand. Abundant research has been dedicated to study dye's adsorption mechanism and to search for a suitable adsorbent [12, 13].

To reach such as goal, several kinds of materials including zeolite, polymers, fly ash, clays and activated carbon have been evaluated as adsorbents for the removal of dyes from contaminated water. However, generally, the major challenges that hinder the fruitful utilization of an adsorbent are the low adsorption capacity, the high cost and the poor recovery. Therefore, growing efforts have been exerted to develop innovative adsorbents that gather the practical advantages of adsorption and overcome the obstacles that limit their effective usage.

Wang et al. investigated the adsorption of methylene blue dye from wastewater by zeolitic material derived from fly ash using different ratios of Si/Al. The experimental data fitted well with the pseudo-second-order model, while the adsorption capacity ranged between 23.20 and 31.90 mg g⁻¹ at 20 °C [14]. Julide Yener et al. reported the adsorption of BY28 on clinoptilolite and amberlite XAD-4. The clinoptilolite displayed higher adsorption capacity (59.6 mg g⁻¹) relative to amberlite XAD-4 that recorded 8.7 mg g⁻¹ [15]. The biosorption of BY28 onto calcined eggshells was reported by Rachid Slimani et al. The kinetics data showed that the adsorption process followed a

pseudo-second-order reaction, whereas the maximum reported biosorption capacity was 28.87 mg/g [16]. Lotfi Mouni et al. studied the removal of methylene blue (MB) by a raw Algerian kaolin sample; the experimental data were analyzed by the Langmuir isotherm, revealing that the maximum adsorption capacity of MB was 52.76 mg/g at 25 °C [17]. Md Tamez Uddin et al. studied the equilibrium and kinetic course of tea waste for the adsorption removal of MB from water. The equilibrium data fitted well with the Langmuir isotherm model with adsorption capacity of 85.16 mg/g; whereas the kinetics of MB adsorption followed the pseudo-second-order kinetic model. Rathinam et al. studied the adsorption removal of basic yellow dye on green alga *Caulerpa scalpelliformis*. The adsorption data showed the adsorption followed a pseudo-second-order kinetic model, whereas the equilibrium data obeyed the Freundlich isotherm model with maximum capacity of 27 mg of the dye per gram of alga, implying a heterogeneous behavior of the adsorbent [18].

MCM-41, one of the most important ordered mesoporous molecular sieves materials, possesses a hierarchical structure with a parallel and ideally hexagonal array of cylindrical pores [19]. The cylindrical shape and the high order of pore symmetry qualify MCM-41 to be effectively used in the selective adsorption and catalysis processes as well as separation of large harmful molecules [20, 21]. Further, the high surface area and the open pore arrangement provide a distinct environment for the removal of hazardous materials (such as dyes). However, like untreated mesoporous silica, MCM-41 material has limited chemical activity due to its particular silica framework of MCM-41 that results in the presence of only few numbers of active sites thus restrict its practical adsorption application. A simple way to activate the mesoporous silica is via introducing a heteroatom in its framework. This way not only improves the physical, chemical properties but also enhances the ion-exchange capacity and generates a large number of active sites [22–25]. Elements of the third main group including B, Al, Ga, In, Tl and some transition metals such as Ti, Fe, Cu, Co, Ni, Ce as well as Zn are considered as the most important candidates for doping the framework of MCM-41 molecular sieves [26–31]. The incorporation of a cation in 3^+ oxidation state such as aluminum, gallium and indium can generate Lewis and Brønsted acidic sites.

Lewis's acid site receives a pair of electrons and forms covalent bonding coordination, whereas Brønsted acidic sites can offer a proton from $-OH$, such as $Si-OH-M^{3+}$ group. The first report of incorporation of Al^{3+} in MCM-41 molecular sieves was reported by Luan et al. [32]. The incorporation process resulted in an increasing number of the acidic sites and enhanced the catalytic activity. The authors concluded that all Al atoms were incorporated in the silica framework in a four-coordinated mode. Doping of the framework of mesoporous silica via cobalt and vanadium was also reported. Substitution of silica by these metal ions resulted in small distortion of the tetrahedral and oxidation of the dopant to higher oxidation states ($Co^{2+} \rightarrow Co^{3+}$ and $V^{4+} \rightarrow V^{5+}$) [33]. Nong-Yue et al. showed that doping of MCM-41 framework by lanthanum increased the hydrothermal and thermal stabilities of Si-MCM-41. However, incorporation of the lanthanum ions (La^{3+}) resulted in a high distortion of the ordered structure [34]. Gallium and indium are considered also as good candidates for doping of the mesoporous silica. Like aluminum, they frequently exist in 3^+ oxidation state, so they can also generate Brønsted acidic sites in the framework [35, 36]. However, the considerably larger radii of Ga(III) and In(III) than that of Si(IV) makes the incorporation of these elements into the MCM-41 framework more difficult than Al(III). Research related to indium-doped mesoporous silica materials are scarce; furthermore, to our knowledge, no research has evaluated the adsorption of BY28 or MB dyes on indium-incorporated MCM-41 materials. In^{3+} has much larger radius of (0.81 Å) than Si^{4+} (0.42 Å); however, synthesizing indium-incorporated MCM-41 is possible using proper synthesis procedures.

In this work, highly ordered MCM-41 was synthesized via a hydrothermal-assisted method. The influence of the introduction of indium on the structural, morphological and textural properties of the MCM-41 framework has been investigated. This route was expected to improve the chemical and physical properties and enhance the ion-exchange capacity through the generation of a large number of active sites [22, 37]. The potential of pure MCM-41 and In-incorporated samples was examined for the elimination of dyes from water. Two basic dyes with different molecular structures, methylene blue (MB) (methylthioninium chloride) and basic yellow (BY) (2-[[[(4-metoksifenil)methyl]hydrazono]methyl]-1,3,3-trimetil-3H-indolium methyl sulfate), were used as

cationic dyes models to investigate the adsorption potential of synthesized materials. The influence of indium content, initial dyes concentration, adsorbent dosage, contact time and pH was investigated. Langmuir, Freundlich and D–R's models were applied to study the equilibrium isotherms of two basic dyes. The suitability of the pseudo-second-order kinetic model for the description of the kinetic data was investigated, from which the adsorption mechanism was examined.

Experimental methods

Materials and experimental methods

Hexadecyl trimethyl-ammonium bromide (CTAB), MW = 364.45, was purchased from ACROS ORGANICS, Belgium. Tetra ethyl orthosilicate (TEOS), $M = 208.33$ g/mol, was purchased from Merck, Germany. Indium (III) acetate and indium (III) oxide, was purchased from STREM CHEMICALS, USA. Sodium hydroxide pellets, $M = 40$ g/mol, was purchased from SIGMA-ALDRICH.

Preparation of pure MCM-41

0.5 gm NaOH was dissolved in dist. H_2O and 7.57 gm CTAB was added and the solution was stirred at 60 °C for 30 min. Then, TEOS was added drop by drop and stirred for 15 min and 2 M NaOH was added to adjust pH at 10. Finally, the solution was transferred into the autoclave at 110 °C for 48 h. The sample was washed with dist. H_2O and ethanol several times, then dried at 70 °C. The sample was calcined at 550 °C for 6 h [38].

Preparation of 0.05 In-MCM-41 (IM0.05)

0.5 gm NaOH was dissolved in dist. H_2O and 7.57 gm CTAB was added and the solution was stirred at 60 °C for 30 min. Then, TEOS was added drop by drop and stirred for 15 min and 2 M NaOH was added to adjust pH at 10. 0.05 M indium acetate was added to the previous solution and stirring for 30 min. Finally, the solution was transferred into the autoclave at 110 °C for 48 h. The sample was washed with dist. H_2O and ethanol several times, then dried

at 70 °C. The sample was calcined at 550 °C for 6 h, and coded IM0.05.

Preparation of 0.1 In-MCM-41 (IM0.1)

0.5 gm NaOH was dissolved in dist. H_2O and 7.57 gm CTAB was added and the solution was stirred at 60 °C for 1 h. Then, TEOS was added drop by drop and stirred for 1 h. 0.1 M indium oxide solution (prepared by dissolving 1.1486 gm of indium oxide in 5 mL nitric acid and 5 mL dist. H_2O at 50 °C for 1.5 h) was added to the previous solution and 2 M NaOH was added to adjust pH at 10. Finally, the solution was transferred into the autoclave at 110 °C for 48 h. The sample was washed with dist. H_2O and ethanol several times, then dried at 70 °C. The sample was calcined at 550 °C for 6 h, and coded IM0.1.

Characterization of pure MCM-41 and indium-incorporated MCM-41

The characterization of the materials was performed using X-ray diffraction (XRD) on (XRD, PANalytical X-ray diffraction equipment model X'Pert PRO). N_2 adsorption/desorption isotherm was analyzed at -196 K °C using NOVA 3200 equipment, USA. The samples were initially out-gassed under vacuum (10^{-4} Torr) at 300 °C O.N. BET surface areas (S_{BET}) were calculated from the adsorption branch of the isotherm by the aid of the BET equation. Pore size distributions (PSD) were estimated using the Barrett, Joyner and Halenda (BJH) method from the adsorption branch of the isotherm. The particles morphology and size were analyzed using a scanning electron microscope with energy-dispersive spectroscopy (SEM/EDS, model Quanta 250 FEG) and transmission electron microscope (TEM, JEOL JEM-2100), whereas the transmittance spectra in the infrared region were obtained with FTIR-ATR Brucker Vertex 80 V with resolution 4 cm^{-1} in the range of $4000\text{--}400\text{ cm}^{-1}$. Diffuse reflectance UV–Vis spectroscopic measurements were taken on a double beam spectrophotometer-JASCO (model V-570 UV–Vis-NIR). The absorption intensity was calculated from the Schuster–Kubelka–Munk equation function $\frac{(1-R_d)^2}{2R_d} = \frac{\alpha}{F_R}$ where F_R is the Kubelka–Munk function corresponding to the absorbance, R_d is the diffuse reflectance and α is the absorption coefficient and the scattering coefficient. The band gap values were

determined using the equation $(\propto h\nu)^{1/\gamma} = A(h\nu - E_g)$ where α is the absorption coefficient, ν is the light frequency, A is the proportionality constant, E_g is the band gap energy and γ is 0.5 and 2 for direct and indirect transitions, respectively.

Adsorption experiments

The prepared samples were evaluated for the adsorption experiments of BY28 and MB by performing batches containing 25 mg of samples in 25 mL of initial concentrations (20–500 mg L⁻¹) of the dye, and these batches were shaken at 250 rpm in a bath shaker at room temperature. The concentration of remaining BY28 and MB was determined employing the maximum absorbance at 439 and 664 nm, respectively, using a UV-Vis spectrophotometer. The removal dye efficiency percentage ($R\%$) was calculated using: $R\% = 100 \times (C_0 - C_e)/C_0$, where C_0 is the initial concentration in ppm and C_e the final concentration in ppm. The adsorption capacity q_e (mg g⁻¹), indicating the amount of adsorbed dye per amount of the dry adsorbent, was determined by the equation: $q_e(\text{mg/g}) = (V \times ((C_0 - C_e)/m))$, where v is the solution volume (L), C_0 the initial concentration (mg L⁻¹), C_e the equilibrium concentration (mg L⁻¹) and m the adsorbent mass (g). The effect of dose was studied using varied dosage of the adsorbent (0.5–1.25 g/L) in 25 mL of 100 ppm of BY28. The effect of pH value on the adsorption process was studied using 25 mL of 100 mg L⁻¹ of BY28 solution on IM0.05 for 180 min, whereas the pH values varied from 4 to 10 and the pH was adjusted with 0.1 M HCL and 0.1 M NH₄OH for acidic and alkaline media, respectively. For kinetic measurements and adsorption isotherms, where the adsorption equilibrium could be reached, the solutions were collected at different intervals in a range of 2–300 min by adsorption of 100 mg L⁻¹ BY28 solutions on 25 mg of IM0.05 sample. The interactive behavior between BY28 molecules and the prepared samples could be revealed by an equilibrium adsorption isotherm which is an important part of the design of adsorption systems so, two common isotherm models were used. Langmuir isotherm indicates that monolayer adsorption is performed on the same sites in the adsorption process. Freundlich model is usually used to indicate adsorption behavior in a heterogeneous

system. These two isotherm models are given as follows

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{b * q_{\max}} * \frac{1}{C_e} \text{ (Langmuir model)}$$

$$\ln q_e = \ln K_f + \frac{1}{n} * \ln C_e \text{ (Freundlich model)}$$

where q_e is the adsorption capacity at equilibrium; $q_{\max}$ (mg/g) is the theoretical maximum adsorption capacity of the dye on samples; C_e (mg/L) is the equilibrium concentration of the dye solution; b (L/mg) represents the Langmuir constant; K_F is Freundlich adsorption constant; and n is an empirical constant which defines kind of isotherms and suggests adsorption extent. Kinetic modeling not only allows the estimation of adsorption rates but also leads to suitable rate expressions and characteristics of possible reaction mechanisms. In this respect, the pseudo-first-order, pseudo-second-order and intra-particle diffusion (IPD) models were used to test the experimental data shown in equations

$$\frac{1}{q_t} = \frac{K_1}{q_1} * \frac{1}{t} + \frac{1}{q_1} \text{ (Pseudo-first-order)}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_2^2} + \frac{t}{q_2} \text{ (Pseudo-second-order)}$$

$$q_t = K_{\text{ipd}} * t^{1/2} + C \text{ (Intra-particle diffusion)}$$

where q_t is the amount of BY28 adsorbed (mg g⁻¹) at time t , q_1 is the maximum adsorption capacity (mg g⁻¹) for pseudo-first-order adsorption, k_1 is the pseudo-first-order rate constant for the BY28 adsorption process (min⁻¹), q_2 is the maximum adsorption capacity for the pseudo-second-order adsorption (g mg⁻¹ min⁻¹), k_2 is the pseudo-second-order rate constant (min⁻¹) and K_{ipd} (mg g⁻¹ min^{-0.5}) is the rate constant of IPD model and C is the boundary layer thickness constant.

Results and discussion

X-ray diffraction

The low-angle XRD patterns for the calcined MCM-41 and In-MCM41 samples are presented in Fig. 1. A well-formed MCM-41 typically exhibits at least three obvious peaks in the range 0.5° and 8° 2 θ . The pure MCM-41 sample showed a set of five prominent peaks referring to a well-formed MCM-41 structure.

Figure 1 **a** Low-angle XRD plot for calcined MCM-41 and indium-incorporated MCM-41 sample and **b** magnified pattern shows the less intense XRD peaks of indium-incorporated samples.

The first three peaks 2.11, 3.71 and 4.28 are related to (100), (110) and (200) Miller indices of a hexagonal unit cell and referring to well-ordered hexagonal mesopores [39]. Two extra peaks, related to 210 and 300 Miller indices, are occasionally detected in exceptionally well-ordered MCM-41. These two peaks are observed at 5.67 and 6.46 indicating successful synthesizing of highly ordered MCM-41. Some variances could be noted comparing XRD spectra of pure MCM-41 and indium-doped samples; as a general trend, there is a broadening of the diffraction peaks accompanied by shifts to higher or lower 2θ degrees. For IM0.05, the most prominent peak labeled as 100 is not as sharp as that of pure MCM-41. Similar conduct was observed for the other four peaks (110), (200), (210) and (300). The less intense diffraction peaks of the indium-doped samples comparing to the pure sample would be related to a wider distribution of pore diameter and less ordering in the arrangement of mesopores. However, the IM0.05 sample still demonstrates the main diffraction peaks along with a distinct peak exhibiting the (210) peak (only seen in remarkably well-ordered samples [39]), although the intensity of the (300) peak is largely reduced, it is still detected (Fig. 1b).

The broadening, loss of some peaks or decline in their intensity are distinctive indications for metal incorporation in the silica framework. Broadening of the diffraction peaks is more pronounced in the IM0.1 accompanied by further loss of the 210 and 300 peaks

intensities (Fig. 1b). The more broadness observed in IM0.1 could be related to the more isomorphous substitution of indium and insertion of higher content of indium in the silica framework [40, 41]. This insertion results in a further disordered arrangement of the channels in the In-incorporated MCM-41 framework; however, the hexagonal structure is still maintained with reasonable regularity. Campos et al. reported similar findings through studying the effect of changing Si:In atomic ratio on the structure of MCM-41 [42]. Another interesting finding that worth to be mentioned is increasing the indium content results in reversing the shift in the diffraction peak positions by about 0.5° (related to pure MCM-41) to lower angle direction. This finding is contrary to the observed shift (by about 0.15° to higher angle direction) in the IM0.05 sample and interestingly referring to unit cell shrinkage at low indium content (IM0.05) and unit cell expansion, consequently an increase in the distance between the pore centers at high indium content (IM0.1). The value of the cell parameter a_0 could afford a good estimation for comparing the pore size diameters of both pure and indium-MCM-41 samples. The low-angle XRD results were applied to calculate the cell parameter ' a_0 ' based on the 2θ value of the (100) peak and Bragg's law: $a_0 = 2d_{100}/\sqrt{3}$. The d spacing of the high-intensity (100) reflection of the parent sample is $41.75 \text{ \AA}$, which is associated with a pore repeat distance, a_0 , of $48.20 \text{ \AA}$. Powder X-ray diffraction of IM0.05 reveals shifting to a lower d spacing; the d spacing of the

(100) reflection decreased to 39.16 Å, which corresponds to a pore repeat distance a_0 of 45.05 Å. The unit cell parameter (a_0) of In-MCM-41 mesoporous molecular sieves is slightly lower than the pristine sample. A framework contraction caused by the small substitution of Si by In could be the origin of this decrease in unit cell parameter. On the other hand, the calculated unit cell parameter (a_0) of IM0.1 displayed a higher value 50.11 Å referring to the expansion of the unit cell. The reasons for increasing/decreasing of the unit cell parameter (a_0) are not so clear; however, it could be related to that MCM-41 lacks firm crystallographic ordering on the atomic level, and the variation of the polymerization degree leads to diverse cell parameters. Due to the easy In-silicate polyanions condensation, the degree of polymerization is not so high to increase the unit cell parameter value at small content of indium. However, at high indium content, the degree of indosilicate polyanions polymerization is enhanced, and consequently the unit cell parameter increases. The primary mesopore diameter (W_d) was calculated using the values of cell parameter according to the equation $W_d = cd\sqrt{(\rho V_p)/(1 + \rho V_p)}$ (the constant 'c' = 1.213, d represents the d -spacing of the (100) peak, ρ refers to the density of the pore wall, and V_p is the volume of a primary mesopore) [43, 44]. Comparing the calculated W_d for pure MCM-41 and In-incorporated samples demonstrated a slight decrease (by 0.27 nm) in IM0.05 and a greater increase (by 0.83 nm) in the IM0.1 sample. The thickness of the pore wall (W_t) was also estimated via the relation $W_t = a_0 - W_d$. A decrease in wall thickness by ~6.5% was observed for IM0.05, and on the other hand the IM0.1 sample showed improvement in the wall thickness by ~20% relative to the pure sample. The enhancement in the extent of indosilicate condensation within the pore wall and consequently the increase in the pore wall thickness could account for reliable improvement in the structural stability.

Nitrogen adsorption–desorption isotherms

Figure 2 depicts the full N_2 adsorption–desorption isotherms for all samples over varying P/P_o pressures from 0.05 to 1.00. All synthesized materials demonstrated type IV isotherms point up to a three-step process: monolayer–multilayer adsorption, then a capillary condensation step, and then a third step ascribed to multilayer adsorption on the outer surface

[45]. The N_2 adsorption–desorption isotherms of pure MCM-41 (Fig. 2a) displayed a typical hysteresis loop in the P/P_o range of 0.30–0.45 relating to capillary condensation within symmetrical mesopores. The sharp slope is a good indication for the high regularity of the pore size, which is consistent with the XRD results. For relative pressures above 0.5, the MCM-41 isotherm shows a nearly steady adsorption region. The specific surface area of the calcined MCM-41 sample was found to be 971 m²/g.

The isotherm of both IM0.05 and IM0.1 (Fig. 2b, c), in comparison with that of the parent MCM-41 material, showed some distinguished variations.

These variations chiefly originated from the multilayer adsorption zone and could be assigned to dissimilar surface properties of pure and incorporated samples (Fig. 2b, c). Firstly, the maximum adsorbed volume is lesser in both IM0.05 and IM0.1 materials; this is in agreement with the lesser surface area values recorded for the two materials. Secondly, the slope related to the capillary condensation step between P/P_o of 0.30 and 0.45 is lesser for IM0.05 than that of the pure material. These findings refer to a wider distribution of pore diameters in the IM0.05 and IM0.01 samples relative to the pure material. An upsurge in the adsorption was detectable at higher relative pressures owing to the formation of adsorbate multilayers on the external surface of the materials. The effect of the pore network is responsible for the type hysteresis loop. IM0.05 showed an H2 hysteresis loop with a triangular shape which refers to the existence of mesopores with narrow mouths (ink-bottle pores). On the other hand, IM0.1 showed an H3 hysteresis loop that does not flatten at P/P_o close to the saturation vapor pressure and referring to slit-like mesopores.

Textural features of the synthesized materials were attained from the adsorption–desorption isotherms results and are depicted in Table 1. The specific surface area was declined from 971 m²/g, in the parent sample, to 482 and 266 m²/g in IM0.05 and IM0.1, respectively. Also, after indium loading, a decline in the BET surface area for both samples was recorded, the decline is more pronounced in the IM0.1 sample which could be assigned a migration of some indium species in MCM-41 framework that could result in blocking of mesopores [46, 47]. Plots of BJH pore size distribution for pure MCM-41 and In-incorporated MCM-41 samples are presented as small windows in (Fig. 2). Both the parent MCM-41 and IM0.05 samples

Figure 2 N₂ adsorption–desorption isotherms and pore size distribution (as windows) of **a** pure MCM-41, **b** IM0.05 and **c** IM0.1 samples.

Table 1 Structural properties of the samples

	d_{100} (Å)	a_0 (nm)	S_{BET} (m ² g ⁻¹)	V_p (cm ³ /g)	D_p (nm)	W_t (nm)
MCM-41	4.17	4.82	971	0.91	2.87	1.95
IM0.05	3.90	4.5	482	1.22	2.82	1.68
IM0.1	5.01	5.79	266	0.47	2.86	2.93

(a_0), average lattice parameter: $a_0 = 2d_{100}/\sqrt{3}$; D_p , Pore diameter determined by the BJH method; W_t , Wall thickness = $a_0 - D_p$

showed a narrow mesopore size distribution; whereas noteworthy variation could be detected in the distributions of pore size in IM0.1 (Fig. 2c). The lower uniformity in the pore size distribution in the IM0.1 sample proposes the existence of a greater disorder in this material, which could be related to an asymmetrical array of the pores and/or the presence of a higher concentration of defects in the pore walls. As expected, the IM0.05 sample recorded smaller pores compared to the other two materials, with an

average pore diameter of 2.82 nm which is slightly lower than the pure (2.866 nm) and IM0.1 (2.864 nm) samples, respectively which is in agreement with the XRD data. The wall thickness was estimated from the relation: $W_t = (2/\sqrt{3}) * d_{100} - \text{BJH_average pore diameter}$. W_t changed from 1.954 nm (in pure MCM-41) to 1.681 and 2.925 nm for IM0.05 and IM0.1 respectively which go in-consistent with results obtained from XRD analysis. It was noticed also that the mesoporous volume (V_p) increased at lower content of

indium (IM0.05), then markedly decreased using high content of indium (IM0.1). There is no regular rule for such variation because MCM-41 has an amorphous structure in which both the bond angle and length are changing. Due to the thin pore wall of MCM-41 relative to other crystalline silica such as zeolites, not all the incorporated metal ions can fully substitute silica into the silica framework [48]. That is, at high indium content, a portion of the indium will be exposed and accumulate at the openings of the pores or unevenly dispersed on the MCM-41 surface. This causes partially blocking of the meso-channels and less adsorption of nitrogen gas so that both the pore volume and the specific surface area decrease with increasing the indium content [49]. On the other hand, if the metal content is not so high, as in IM0.05 sample, the probability for metal ions to accumulate on the surface is low, alternately the metal ions can only incorporate deep within the silica framework, so the decline of V_p might not happen and might be increased due to the increased indium-oxygen bond [48].

Scanning electron microscope and EDX

Figure 3 depicts the scanning electron microscope (SEM) images of MCM-41 and In-MCM-41 samples. The morphology of a characteristic MCM-41 is shown in Fig. 3a, b. The low magnification image (Fig. 3a) reveals a variety of elongated rod-like and spherical morphologies. These morphologies are distinctive for synthesized MCM-41 in basic media [50, 51]. At a high magnification scale (Fig. 3b), typical symmetrical sphere-like particles are obviously seen. The average diameter of the spherical particle was estimated to be within the 600 and 700 nm range. The SEM image of IM0.05 (Fig. 3c) illustrates that the material retains the mesoporous character, with a uniform particle size distribution and a wormy morphology. Higher magnification showed that the particles have a sacks-like shape encompassing several tiny particles. The large particles form a skeleton built up from grains interconnected through tunnels. The width of these particles is in the region of 100–200 nm. On the other hand, the SEM image of

Figure 3 SEM images of the **a** pure MCM-41 (low magnification), **b** high magnification, **c** IM0.05 and **d** IM0.1.

IM0.1 (Fig. 3d) exhibited aggregated irregular nearly spherical particles with an interconnected network. The higher indium doping content may cause a partial collapse of the pore structure and the presence of such irregularity in this sample. The energy-dispersive X-ray (EDX) spectroscopy of IM0.05 and IM0.1, shown in (S1, supplementary material), confirmed the existence of O, Si and In elements with no other impurities. The atomic percentage of In: Si equals to 8.18% in the IM0.1 sample, which is very close to the calculated value of $\text{In/Si} = 10\%$.

Transmission electron microscopy

The TEM images of pure MCM-41 and In-incorporated samples are shown in Fig. 4. TEM of the parent sample plainly showed some key features of MCM-41 (Fig. 4a). The silica microspheres displayed a pseudo-periodic lattice of a parallel bundle of pores. Figure 4b shows uniform lines in the vertical direction of the pore channels referring to a long-range ordered structure of the one-dimensional channels of MCM-41 structure and which matches well with the XRD results. The distance separated between the centers of lighter spots represents the cell parameter ' a_0 '. This distance was measured between at least 50 centers; the average value was found to be 4.46 ± 0.06 nm. This result is well in line with the average value determined via X-ray diffraction in Table 1 ($a_0 = 4.67 \pm 0.09$ nm). The average pore diameter was estimated from the TEM image assuming that the average thickness of the pore wall (W_p) is 0.68 nm (Table 1). This value was found to be 3.78 ± 0.06 nm and falls within the acceptable range for calcined MCM-41 [43, 52, 53]. The TEM image of IM0.1 sample shown in (Fig. 4e, f) presented a similar pore shape related to the pure MCM-41 sample. However, partially irregular pore-ordering and morphological defects were observed which probably related to a partial collapse of the structure of MCM-41 due to the high loading amount of indium. The hexagonal array and the regularity of the pore channels are more pronounced in the TEM image of IM0.05. A distinctive hexagonal pore structure depicting each pore surrounded by six neighbors is clearly observed in Fig. 4d. This confirms the highly long-range well-ordered hexagonal structure of IM0.05 sample and is in good agreement with both XRD and isotherms textural results. The average cell parameter ' a_0 ' determined by measuring the separation distance

between centers of the lighter spots was 4.20 ± 0.019 and 4.87 ± 0.057 nm for IM0.05 and IM0.1 samples, respectively (Fig. 5). These values are in good matching with the average cell parameter values (4.50 and 5.01 Å) calculated from XRD (Table 1). The IM0.05 image also showed a series of parallel lines of alternating dark and light (parallel fringes) representing the repeating pattern of MCM-41 pores (Fig. 4d). The cell parameter (a_0) could be estimated by measuring the length between middles of successive, brighter parallel lines. The average cell parameter was calculated as 4.27 ± 0.10 nm; this value is very consistent with the value (4.20 ± 0.019 nm) obtained by measuring the separation distance between 50 pore centers and is about 3.6% lower than the average cell parameter value calculated via XRD results (Table 1). The average pore diameter W_d of IM0.05 estimated from the TEM image is 5.9% smaller than W_d calculated for the pure sample. These varied values are consistent with the difference between pore widths of the parent material and indium-incorporated MCM-41 sample calculated based on the XRD results.

Optical properties and band gap

Figure 6 shows the UV/vis absorption spectra of the samples attained via application of the Kubelka–Munk formula to the diffuse reflectance spectra. When compared to pure MCM-41, indium-incorporated materials demonstrated stronger absorption bands in the UV region range. Furthermore, redshifts of the absorption edge in the visible and near-visible region related to charge transfer transition $\text{O}^{2-} \rightarrow \text{In}^{3+}$ were observed [54–56]. These results are good proofs for the incorporation of indium into the silica framework; similar findings were reported by Agger et al. [57]. Moreover, the greater absorption intensity of the 0.1In-MCM spectrum could be related to the higher indium content in this sample. The UV–Vis diffuse reflectance spectra of IM0.05 exhibited two absorption bands at ~ 255 and 321 nm related to In^{3+} in tetrahedral and hexacoordinated mode. Both indium-incorporated samples revealed an absorption shoulder at 342 nm, which signifies the presence of some polymeric indium species (In–O–In). Yun Hu et al. reported similar findings with absorption shoulder at 350 nm through the incorporation of vanadium into the MCM-41 at 3.6 wt% [58]. The absence of absorption band in the region longer than

Figure 4 The HRTEM images of MCM-41 **a** honeycomb structure, **b** well-ordered pattern. The HRTEM images of IM0.05, **c** honeycomb-hexagonal array, **d** well-ordered pattern.

400 nm indicates the high dispersion In-oxide species and there is no aggregated In-oxide species [59].

The HRTEM images of IM0.1 with partially disordered channels, **e** low magnification and **f** higher magnification.

The absorption edge of the pure and In-incorporated MCM-41 samples has different positions, which could consequently be used in the calculation of the

Figure 5 Histogram represents the average cell parameter ' a_0 ' **a** pure MCM-41, **b** IM0.05 and **c** IM0.1.

Figure 6 Diffuse reflectance UV–Vis spectra of pure MCM-41 and In-incorporated samples.

band gaps and obtaining vital information about the indium heteroatom-incorporated MCM-41. The direct band gap energy values (E_g) of samples have been calculated via the application of Kubelka–Munk formula and plotting $(F_R/h\nu)^2$ versus $h\nu$ and extrapolating the slopes to $(F_R/h\nu)^2 = 0$ (Fig. 7). The pure MCM-41 sample recorded an optical band gap of 5.79 eV while the 0.05 In-MCM and 0.1 In-MCM displayed band gap values of 3.28 and 4.10 eV, respectively. The higher band gap values of indium-incorporated MCM-41 than the metal oxide counterpart (2.7–2.9 eV) [60–62] indicate high dispersion of

the heteroatom in the siliceous framework [63]. These results go consistent with those reported by Casas-Orozco et al., who showed that the high dispersal of metal oxide in silica matrix results in reducing their band gaps [63].

Infrared spectra

The infrared spectra of the pure and In-incorporated MCM-41 are depicted in Fig. 8. The samples showed bands in the region of 400–4000 cm^{-1} characteristic to the vibration of the MCM-41 structural network and consistent with the literature [64, 65]. The uncalcined sample demonstrated a strong absorption band at 3729 cm^{-1} assigned to vibration of free νSiOH groups [66, 67]. Another broad absorption band was observed at 3421 cm^{-1} which could be ascribed to the vibration of hydrogen-bonded $\nu(\text{SiOH})$ groups disturbed by adsorbed water [66, 68]. A group of bands was observed around 2915, 2849, 1617 and 1480 cm^{-1} . The bands at 2915 and 2849 cm^{-1} are assigned to $\text{CH}(\text{CH}_3)$ and $\text{CH}(\text{CH}_2)$ stretching modes, respectively. The peaks observed at 1617 cm^{-1} are assigned to $\text{H}_2\text{O}_{\text{ads}}$ molecules, whereas the peak at 1480 cm^{-1} is ascribed to the bending modes of $\delta\text{CH}(\text{CH}_3)$ and $\delta\text{H}(\text{CH}_2)$ groups. The band set shown at 960, 910 and 719 and 450 cm^{-1} is assigned to the vibration of MCM-41 framework [69]. For the calcined pure MCM-41 (Fig. 8), the bands at 2915 and 2849 and 1480 cm^{-1} disappeared referring to the

Figure 7 Plot of $[F(R)hv]^2$ versus energy ($h\nu$) of and optical band gap calculation from Kubelka–Munk equation: **a** pure MCM-41, **b** IM0.05 and **c** IM0.1.

Figure 8 **a** FT-IR spectra (400–4000 cm^{-1}) and **b** magnified FT-IR spectra (400–1400 cm^{-1}) of CTAB surfactant, pure MCM-41 before calcination and MCM-41, IM0.05 and IM0.1 after calcination.

complete removal of the CTAB template. After calcination, the framework of mesoporous silica was formed, which could be further proved by (a) varying shifts to lower and higher wavenumbers and (b) appearing of new bands associated with the external and internal, symmetric and asymmetric Si–O stretching vibrations [70]. The emerging of new bands at 1238 and 1060 cm^{-1} is assigned to asymmetric (Si–O–Si)_{as} while the band at 966 cm^{-1} is assigned to $\nu_{\text{ass}}(\text{SiOH})$. The band observed at 800 cm^{-1} is related to $\nu_{\text{as}}(\text{Si–O–Si})$, and the well-defined bands at 566 and 445 cm^{-1} are characteristic to

bending mode of siloxane $\delta(\text{Si–O–Si})$. For In-incorporated samples IM0.05 and IM0.1 (Fig. 8), the transmittance intensity of 3436, 1627 cm^{-1} bands of pure MCM-41 decreased and little shifted toward higher wavenumbers, 3440 and 1631 cm^{-1} respectively. Although the band shift is not high, it could be considered as a good proof for the incorporation of In in the MCM-41 pores and consistent with earlier reports [71, 72]. Also, the band at 1060 cm^{-1} in pure MCM-41 was shifted to 1062 cm^{-1} in IM0.05 and IM0.1 samples. Moreover, a change was detected in the intensity of the 966 cm^{-1} peaks upon increasing

the indium content indicating a structural change in the surface Si–OH group. Increasing the indium content results in the introduction of further indium atoms in the silica framework and the formation of new vibration bands, as (Si–O–In). Similar observations were reported for the incorporation of zinc and cerium in the framework of MCM-41 [69, 73]. So, the apparent variation in the intensity of the silanol groups bands basically refers to the incorporation of indium in the MCM-41 framework [74]. Furthermore, the bending band at 445 cm^{-1} was subjected to changes in intensity and little shifted to higher wavenumbers after introducing indium atoms into MCM-41. Combining the data obtained from small-angle XRD, TEM, SEM and surface area and porosity analyses, we can conclude that indium enters the skeleton of the MCM-41 molecular sieve to form In-MCM-41.

Adsorption studies

Effect of indium presence on BY28 and MB adsorption

The adsorptive removal ability of pure MCM-41, IM0.05 and IM0.1 for BY28 and MB was investigated and is depicted in Fig. 9. The incorporation of indium into the MCM-41 structure remarkably enhanced the BY28 dye removal competency in comparison with the pure MCM-41. The pure MCM-41 showed moderate affinity to remove both BY28 and MB dyes with removal efficiency 66.5 and 51.5%, respectively. Both IM0.05 and IM0.1 samples showed almost the same high affinity to remove BY28 from aqueous solution with removal efficiency 88.2 and 90.3%, respectively, whereas, for the MB dye, the IM0.1 sample showed

Figure 9 Effect of indium presence on BY28 and MB adsorption.

the highest removal efficiency (90.9%). The varying affinity of the samples for adsorption of the two dyes could be related to the different molecular structures of BY28 and MB and the type of bonds they form with the adsorbent surface. The following experiments will focus on the study of the factors affecting on the adsorption of the BY28 dye.

Effect of initial dye concentration

The observed adsorption increased with the increment of BY28 concentrations until the equilibrium is reached. The effect of initial concentration on adsorption competency was investigated using a varying initial concentration of BY28 ($20\text{--}500\text{ mg L}^{-1}$). The adsorption capacities of pure MCM-41, IM0.05 and IM0.1 samples are depicted in Fig. 10a. At a low initial concentration of dye, the adsorbent materials are capable to eliminate the majority of dye. For BY28 at 20 mg L^{-1} , the adsorption removal was 95.9, 95.5 and 96% for pure MCM-41, IM0.05 and IM0.1, respectively. This could be related to that the low initial dye concentration provides the driving force essential to overcome the resistance force to transference of dyes from the aqueous solution to MCM-41 and/or In/MCM-41 samples [75]. On the contrary, the elimination efficiency reduced at high initial dye concentration which could be assigned to the high initial numbers of dye molecules far exceeds the accessible active surface sites of the adsorbents [23].

Adsorption isotherms

Figure 10b–d shows the results of Langmuir and Freundlich fitting with the experimental data of BY28 adsorption on the prepared adsorbents. Table 2 lists the Langmuir and Freundlich constants and important coefficients for these two models. The model fitting to our experimental data is assessed by the linear regression values; the value R^2 is referring to the degree of a model fits experimental data. As shown in Table 2, according to the R^2 , the adsorption of BY28 molecules on the synthesized samples well-fitted with the Langmuir model indicating the establishment of monolayer coverage of the BY28 molecules on the outer and inner surfaces of the adsorbents. This also refers that the competition of the solvent and the adsorbate to attach the adsorbent sites is not strong and indicates the high efficiency of

Figure 10 **a** Effect of initial BY28 concentration, adsorption isotherms of BY28 on pure and indium-incorporated samples, **b** Langmuir, **c** Freundlich and **d** D–R models.

Table 2 Adsorption isotherm parameters of Langmuir, Freundlich and D–R isotherm models for BY28

Samples	T (°C)	Langmuir isotherm model			Freundlich isotherm model			D–R isotherm model				
		$q_{\max}$ (mg g ⁻¹)	B (L mg ⁻¹)	R^2	K_F (mg g ⁻¹)	N	R^2	q_D (mmol g ⁻¹)	B (mol ² kJ)	R^2	E (kJ mol ⁻¹)	R^2
MCM-41	25	123.46	0.230	0.971	21.407	2.611	0.944	2.454	0.0008	0.970	25.0	0.970
IM0.05	25	156.99	0.154	0.997	23.804	2.515	0.957	2.398	0.0007	0.982	26.7	0.982
IM0.1	25	158.48	0.174	0.997	28.419	2.647	0.934	2.254	0.000008	0.885	250	0.885

synthesized samples to adsorb BY28 dye [76]. The indium-incorporated samples, IM0.05 and IM0.1 showed higher BY28 adsorbing capacity (156.99 and

158.48 mg g⁻¹, respectively) in comparison with the pure sample (123.46 mg g⁻¹). Based on the good dye removal affinity, the high adsorption capacity and the

long-range well-ordered structure of IM0.05, the following experiments will be carried out using this sample. By comparing the adsorption capacities of the synthesized adsorbents with some adsorbents reported in the literature (Table 3), it can be observed that the synthesized adsorbents are among the most effective materials for adsorption of BY28 dye.

Dubinin–Radushkevich (D–R) model was used to examine the adsorption process and differentiate between chemical and physical adsorption, according to the following equation [77]:

$$\ln q_e = \ln q_D - \beta \varepsilon^2$$

q_e is the adsorption capacity of the dye on IM0.05 adsorbent at equilibrium (mmol g^{-1}); q_D is the D–R adsorption capacity (mmol g^{-1}); β ($\text{mol}^2 \text{kJ}^{-2}$) is the activity coefficient depending on average energy of adsorption; ε is the Polanyi potential obtained by the equation:

$$\varepsilon = RT \left(1 + \frac{1}{C_e} \right)$$

R is the gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$), C_e is the equilibrium concentration of BY28 dye (mol L^{-1}) and T is the absolute temperature (K). A straight line is obtained by plotting $\ln q_e$ versus ε^2 ; the slope of this line is β and the intercept equal $\ln q_D$ (Fig. 10d). The average free energy (kJ mol^{-1}) could be obtained according to the relation:

$$E = \frac{1}{\sqrt{2\beta}}$$

The value of E (kJ mol^{-1}) provides a good sign for the type of adsorption process, whether it is physical or chemical. The calculated average free energy for adsorption of BY28 on IM0.05 was found to be greater than 8 kJ mol^{-1} (26.7 kJ mol^{-1}) (Table 2) referring to that the adsorption of BY28 on IM0.05 adsorbent is chemical adsorption.

Effect of adsorbent dosage

The effect of adsorbent IM0.05 dose on the BY28 removal is shown in Fig. 11a. The adsorption capacity of BY28 increased significantly by varying the adsorbent dose from 0.5 to 1.0 g/L. After the dose reached 1.0 g/L, the adsorption of BY28 reached the maximum capacity (88.23 mg g^{-1}). The adsorption capacity declined (44.42 mg g^{-1}) when the dose further increased up to 1.25 g/L. The higher adsorption capacity at low dosage could be explained by the great availability of all surface-active sites for the adsorption process. So, the surface becomes saturated faster, thus leading to a high adsorption capacity. On the other hand, at higher adsorbent dose, a large portion of low-energy sites becomes occupied, so there is a decrease in the availability of high-energy sites thus leading to a low dye-adsorption capacity. Also, the possibility of adsorbent particles collision

Table 3 Adsorption capacities of some adsorbents compared to IM0.05 for the removal of BY28 dye

Adsorbent	q_m (mg g^{-1})	References
Activated carbon	77.70	[78]
Clinoptilolite	8.70	[15]
Boron industry waste	75.00	[79]
Calcined eggshells	28.87	[16]
Amberlite XAD-4	11.70	[15]
Clinoptilolite	52.90	[15]
Kaolin	16.23	[80]
Green alga	27.00	[18]
Sepiolite	31.50	[81]
Bentonite	256.4	[82]
Smectite	76.92	[83]
Calcined mussel shells	14.60	[84]
Conch shells	34.10	[85]
Coal-based granular activated carbon	3.83	[86]
Tea waste	34.88	[87]
MCM-41	123.50	Present study
IM0.1	158.70	Present study
IM0.05	156.99	Present study

Figure 11 Effect of **a** dosage and **b** pH of BY28 adsorption on IM0.05.

elevated at a high adsorbent dosage could lead to aggregation of the particles and a reduction in the adsorbent surface area. According to these findings, 1 g/L of the adsorbent dosage was applied as the optimal dose for the adsorption study.

Effect of pH

The initial pH value has a substantial operational influence on the adsorption competence of adsorbents. Figure 11b shows that the adsorption of BY28 was enhanced by pH increment till pH 10. BY28 is a cationic dye whereas IM0.05 is negatively charged at pH high than the isoelectric point [88]. At low pH, the excess H^+ competes with the cationic BY28 dye for adsorption sites which resulted in the low adsorption of BY28 in the acidic medium [89]. Raising the solution pH to 8 resulted in a remarkable increase in BY28, this could be assigned to the decrease of electrostatic repulsion between positively charged BY28 molecules and negatively charged IM0.05 surface which could lead to an increase in dye adsorption availability [90]. The IM0.05 surface has a large number of silanol groups Si-OH, and raising the pH of the medium leads to more deprotonation of the Si-OH groups to Si-O $^-$. The latter form has more affinity to form strong electrostatic interaction with BY28 cationic dye [91]. Moreover, the (Si-OH) silanol groups on the surface of IM0.05 could also form hydrogen bonding with the amine groups of BY28 molecules [92]. Further pH increasing resulted in diminishing of the dye adsorption by about 20% (at pH 10). The obvious decline of the adsorption capacity of BY28 at either low or high pH values

could be related to the dissolution or structure instability of MCM-41 in strong acidic or alkaline media [12, 93].

Effect of contact time and adsorption kinetics

Figure 12a shows that about half of the BY28 dye (49.7%) was eliminated by IM0.05 through only 2 min. There is a slight increase in the adsorption up to 90 min, then a further increase in the dye adsorption to reach a maximum of adsorption capacity of 88.23 mg g^{-1} in 180 min and finally the adsorption reached to equilibrium supported by appearance of a plateau in adsorption curve. The fast initial adsorption rate could be interpreted by the high number of available active sites on the surface of IM0.05 adsorbent, this would lead to increasing the concentration gradient between adsorbed BY28 molecules on the IM0.05 surface and in the solution, whereas the slow adsorption rate after that would be related to agglomeration of BY28 molecules on the active sites of the adsorbent. The adsorption kinetic of BY28 on IM0.05 was studied at pH 5.6, 25°C using an initial concentration of 100 mg L^{-1} . The pseudo-first-order, pseudo-second-order and intra-particle diffusion (IPD) models (Fig. 12b–d) were applied to estimate the adsorption rate, obtained rate parameter characteristics to a possible reaction mechanism. Table 4 presents the calculated kinetics correlation coefficients and constants. The pseudo-second-order model was found to best-fit than the pseudo-first-order model with ($R^2 > 0.9671$). The adsorption process was proposed to be governed by chemical adsorption involving an exchange or/and sharing

Figure 12 a Effect of time and b–d kinetic models for adsorption of BY28, b pseudo-first-order, c pseudo-second-order and d intra-particle diffusion.

Table 4 Kinetic parameters for BY28 adsorption on IM0.05

Pseudo-second order	q_2 (g mg ⁻¹ min ⁻¹)	86.2
	K_2 (g mg ⁻¹ min ⁻¹)	0.001
	R^2	0.9671
Pseudo-first order	q_1 (mg g ⁻¹)	212.4
	K_1 (min ⁻¹)	0.0655
	R^2	0.3362
Intra-particle diffusion	C (mg g ⁻¹)	26.05
	K_{ipd} (mg g ⁻¹ min ^{-0.5})	4.73
	R^2	0.7718

electrons between adsorbate and adsorbent surface. The estimated initial adsorption rate was found to be 0.001 (g mg⁻¹ min⁻¹), which could be related to the IM0.05 structure and the type of the active sites.

Recovery and regeneration of adsorbent

To examine the recovery potential of the adsorbent, recycle experiments were implemented for three subsequent adsorption–desorption cycles. After each adsorption, the sample was recovered through washing by 0.1 M NaOH solution. Then, the recovered adsorbent was reutilized in the next cycle using the same conditions; the BY28 adsorption results are illustrated in Fig. 13. It could be observed that IM0.05 could adsorb BY28 efficiently even after reusing for three times. The removal percentage somewhat diminished from 88.23% in the first cycle to 78.65% in the third cycle, perhaps because during the recycling experiments, a slight remnant of the BY28 dye still existed on the IM0.05 surface [94]. Overall, the IM0.05

Figure 13 Reusability of IM0.05 for removal BY28 for three cycles.

adsorbent could be reused for several cycles while preserving good adsorption activity.

Possible adsorption mechanism

The possible interactions between the adsorbents and the dye molecules in the aqueous solution could be ascribed to some adsorption mechanisms, such as electrostatic interaction, hydrogen bonding, acid-base interaction, coordination and ion exchange. BY28 dye has an intricate chemical structure with some functional groups, such as =N–C, phenyl- and =N–N, presenting multiple possible interactions locations between the BY28 molecules and the adsorbents. At low pH values (less than the pHZPC value), the acidic medium gives more protons, consequently imparting the surface of the adsorbent a net positive charge. The lower adsorption capacity observed at such values is a direct result to the electrostatic repulsion between the positively charged active sites on the adsorbent and the cationic BY28 dye molecules. Conversely, the adsorbent surface is negatively charged above the pHZPC. The adsorption of the BY28 dye molecules on the unmodified sample could be attributed to weak van der Waals interactions as well as the hydrogen bonding between the BY28 molecules and the walls of the mesopores. The presence of silanol groups and partial negative charges on silica surface favors the formation of hydrogen bonding, and weak van der Waals interactions with the nitrogen atoms of the dye, which ultimately resulted in maximum sorption capacity of 123.46 mg g^{-1} . On the other hand, in this study, although the indium-incorporated samples have lower surface area and pore volume (Table 1), they have much higher BY28 adsorption capacity than the pure sample. This observation led to the conclusion

that the weak hydrogen bonding and van der Waals interactions are not the principal driving forces of adsorption. A plausible mechanism could be related to the immobilization of indium species generates more negative sites (i.e., both O^- and In^-) on the wall of In–MCM-41, which causes more adsorption of BY28 dye molecules according to the following equations.

The increased negative charges on the pore surface provides more opportunities for electrostatic attraction to the positive charge of BY28 ions (Scheme 1). The YB^+ parts of the dye could find more opportunity to interact via electrostatic interactions with the increased positive charges induced by In-incorporation in addition to this electrostatic interaction, the N-groups could also interact with the silanol groups present on the surface of the mesoporous silica by hydrogen bonding.

Conclusion

Pure MCM-41 and In-MCM-41 mesoporous materials with Si/In = 95 and 90 were synthesized using a hydrothermal-assisted method; TEOS, indium acetate and indium oxide as the silica and indium sources, respectively. The synthesized materials were structurally and morphologically characterized using XRD, N_2 adsorption–desorption, SEM–EDX, TEM, diffuse reflectance (DR) and FTIR. The results showed successful incorporation of indium into the framework of MCM-41 and the indium doping percentage has a great impact on the structural, morphology and textural properties of the MCM-41. It was interestingly found that low indium content (5%) resulted in shrinkage of unit cell while increasing the indium content to 10% led to reverse effect and expansion of the unit cell. Using a high amount of indium (In/Si = 10%) may lead to a partial collapse of MCM-41 structure. On the other hand, the IM0.05 sample synthesized at (In/Si = 5%) showed remarkable highly ordered pore structure. XRD confirmed the well-ordered structure of pure and IM0.05 samples by showing diffractions peaks related to (210)

Scheme 1 Possible adsorption mechanism of BY28 on MCM-41 and IM0.05 adsorbents.

(300) which are distinctive to a long-range highly ordered MCM-41 structure. Furthermore, the morphological study showed a distinctive highly ordered hexagonal pore structure which is in good agreement with both XRD and the textural isotherms results. The adsorption capability of the materials was evaluated for the removal of MB and BY28 dyes from aqueous solution. The impact of initial dye concentration, adsorbent dose, pH and contact time was investigated. The adsorption of BY28 by pure and In-incorporated samples fitted well with the Langmuir equilibrium isotherm with adsorption capacity of 123.46, 156.99 and 158.48 mg g^{-1} for pure, IM0.05 and IM0.1 samples, respectively. The calculated free adsorption energy obtained from the D–R isotherm was found to be 26.7 kJ mol^{-1} referring to that the adsorption of BY28 on IM0.05 adsorbent is chemical adsorption. The adsorption kinetics of BY28 on IM0.05 followed the pseudo-second-order model. The adsorption results demonstrated that the synthesized materials are efficient adsorbents for the removal of MB and BY28 cationic dyes from aqueous solutions. The reusability of the IM0.05 was tested for three subsequent adsorption–desorption cycles; it was observed that IM0.05 could adsorb BY28 efficiently even after reusing for three times. A plausible mechanism for the high adsorption of the indium-incorporated samples could be related to that the immobilization of indium species generates more negative sites (i.e., both O^- and In^-) on the wall of In-MCM-41; the increasing negative charges on the pore surface provides more opportunities for electrostatic attraction to the positive charge of BY28 ions.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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