



Modified Nanoporous Carbon Material for Anionic Dye Removal from Aqueous Solution

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ABSTRACT

In this study, the adsorption behavior of anionic dyes from aqueous solution onto mesoporous carbon material (CMK-1) and modified with polymer (PANI/CMK-1) has been investigated as a function of parameters such as adsorbent dose (0.08-0.8 g/L), solution pH 3–10, contact time and initial concentration (10-100 mg/L). The influence of these parameters on the adsorption capacity has been studied using the batch process. The experimental data were analyzed by the Langmuir, Freundlich and Temkin isotherms. The adsorption isotherm was found to follow the Freundlich model. The structural order and textural properties of the synthesized materials were studied by XRD, SEM, and nitrogen adsorption-desorption analysis. The characteristic results indicated that the modification was successfully done. This study showed that modified nanoporous carbon materials are excellent adsorbents for the removal of anionic dyes from wastewater.

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1. INTRODUCTION

Wastewater coming out from the textile industries causes major hazards to the environment due to the presence of a large number of contaminants. Removal of dyes from wastewater is the main problem encountered in textile industry. Over 50,000 tons of dyes are discharged into environmental effluent annually, producing health risk and damage to aquatic and vegetal life [1]. Most dyestuffs are classified according to their solubility, coloring properties, and chemical structure. After coloring is completed, the waste ought not to be discharged into the environment without purification, because dyestuffs are carcinogenic. These compounds can contaminate underground water in trace amounts by leaking from soil and pose a very great risk to human health over a long period of time. Dyes are usually stable to photo-degradation, biodegradation and oxidizing agents [2], which has led to intensive investigations on physical or chemical methods to remove these dye from wastewater. These studies include the use of coagulants [3], ultra-filtration [4], electro-chemical methods [5, 6] and adsorption methods, which are the most widely used techniques [7-11]. The advantages and disadvantages of each

technique have been extensively reviewed [12]. Amongst the physical methods available, adsorption process is one of the most efficient methods to remove dyes, pigments and other colorants from wastewater. It is well known that adsorption is based on equilibrium separation process. The common adsorbents primarily include activated carbons, zeolites, clays, industrial by-products, agricultural wastes, biomass and polymeric materials [13]. However, these adsorbents described above suffer from low adsorption capacities and separation inconvenience. Therefore, efforts are still needed to carry out investigation for new promising adsorbents. For example Activated carbons prepared by activation of biomass are fundamentally microporous [14], which limits their adsorption capacity of dyes since dyes are bulky molecules with sizes of over 1 nm [15-17]. Therefore, carbons with mesoporous structures are advantageous [18-21]. Mesoporous (2–50 nm) carbon which has open pore structure and large pore size provides marked advantage in bulky molecular adsorption [22, 23]. In this work, highly ordered mesoporous carbon molecular sieves designated as CMK-1 were synthesized using mesoporous MCM-48 silica with various pore diameters as template and then modified by polyaniline. The structural order and textural properties of the synthesized materials have been studied by XRD, SEM and Nitrogen adsorption-

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desorption analysis. The present work deals with the adsorption of anionic dyes (such as: methyl orange (MO) and methyl red (MR)) from aqueous solutions on a new Nano sorbent; ordered mesoporous carbon coated with polyaniline (PANI/CMK-1) material. It has been found that PANI/CMK-1 shows good adsorption for anionic dyes. Batch adsorption studies were carried out to study the effect of various parameters like adsorbent dose, pH, and initial concentration and contact time. Freundlich and Langmuir adsorption isotherms were used to model the equilibrium adsorption data for anionic dyes.

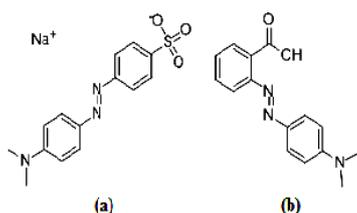


Figure 1. Chemical structure of anionic dyes, (a) methyl orange (MO), (b) methyl red (MR).

2. EXPERIMENTAL

2. 1. Synthesis of Mesoporous Silica (MCM-48)

MCM-48 was prepared according to the synthesis procedure described by Shao et al. [24]. In a representative synthesis, the MCM-48 molecular sieve was prepared as follows: 10 ml of tetraethyl orthosilicate was mixed with 50 ml of deionized water, and the mixture was vigorously stirred for 40 min at 308 K, then 0.9 g of NaOH and 0.19 g of NaF were added into mixture at the same time. After completing NaF addition, the required content of sources were added. After another 60 min of vigorous stirring, 10.61 g of cetyltrimethylammonium bromide was added to the mixture, and stirring continued for 60 min. The mixture was heated for 24 h at 393 K in an autoclave under static conditions, and the resulting product was filtered, washed with distilled water, and dried at 373 K. The as-synthesized samples were then calcined in air for 4 h at 823 K, increasing the temperature to 823 K at 1 °C/min of the heating rate.

2. 2. Synthesis of Mesoporous Carbon (CMK-1)

CMK-1 was prepared by using MCM-48 material as template and sucrose as the carbon source. In a typical synthesis of mesoporous carbon, 1 g of template (mesoporous silica material) was added to a solution obtained by dissolving 1.25 g of sucrose and 0.14 g of H₂SO₄ in 5 g of water, and keeping the mixture in an

oven for 6 h at 373 K. Subsequently, the oven temperature was raised to 433 K for another 6 h. In order to obtain fully polymerized and carbonized sucrose inside the pores of the silica template, 0.8 g of sucrose, 0.09 g of H₂SO₄ and 5 g of water were again added to the pretreated sample and the mixture was again subjected to the thermal treatment described above. The template-polymer composites were then pyrolyzed in a nitrogen flow at 1173 K and kept under these conditions for 6 h to carbonize the polymer. The carbon-silica composite thus obtained was washed with 1 M NaOH solution of 50% ethanol-50% H₂O twice at 363 K, in order to dissolve the silica template completely. The carbon samples obtained after the silica removal were filtered, washed with ethanol and dried at 393 K [25].

2. 3. Preparation of PANI/CMK-1 Composites

2.55 g of CMK-1 was immersed in a solution containing 2.5 ml of aniline, 5 ml of 6 mol/L hydrochloric acid (HCl) and 50 ml of water. After stirring for 30 min, an ammonium persulfate (APS) solution containing 25 ml of water and 5.7 g of APS was added drop wise at 273 K and stirring continued for a further 3 h. The resulting product was filtered and washed repeatedly with acetone, HCl and deionized water, respectively. Finally, the resulting composite was dried under vacuum at 373 K for 24 h.

2. 4. Characterization

The X-ray powder diffraction patterns were recorded on a Philips 1830 diffractometer using Cu K α radiation. The diffractograms were recorded in the 2 θ range of 1–10 with a 2 θ step size of 0.018° and a step time of 1 s. Adsorption-desorption isotherms of the synthesized samples were measured at 77 K on micrometrics model ASAP 2010 sorptometer to determine an average pore diameter. Pore-size distributions were calculated by the Barrett-Joyner-Halenda (BJH) method, while surface area of the sample was measured by Brunauer-Emmet-Teller (BET) method. SEM images were obtained with JEOL 6300F SEM and the Fourier transform infrared spectra for the unmodified and modified samples were measured on a DIGILABFTS 7000 instrument under attenuated total reflection (ATR) mode using a diamond module.

2. 5. Dye Adsorption Studies

To study the effect of important parameters like the pH, contact time, initial dye concentration and adsorbent dose on the adsorptive removal of anionic dyes, batch experiments were conducted. In each batch, the mixture of 25 ml dye solution of known pH, concentration and a known amount of adsorbent was taken in 50 ml stoppered conical flask. The resulting mixture was continuously

shaken in a shaking bath with a speed of 160 shakes/min at 293 K for 2 h until equilibrium was reached. The concentration of methyl orange and methyl red in the supernatant was determined with a UV spectrophotometer (UV mini 1240 shimadzu) with the wavelength at 470.5 and 451 nm, respectively. The effect of solution pH on anionic dyes removal was investigated over a pH range of 3–10. The pH was adjusted using 0.10 M HCl or 0.10 M NaOH aqueous solution. The experiments were also done by varying the amount of adsorbents (0.002–0.02 g / 25 ml) and the concentration of dye solution (10–100 mg/L). For adsorption isotherm, dye solutions of different concentrations (10–100 mg/L) were shaken with the known amount of adsorbent (0.01 g) till the equilibrium was achieved. Then, the residual MO and MR concentrations of the solution were determined. The amount of adsorbed anionic dyes per gram PANI/CMK-1 at equilibrium, q_e (mg/g), was obtained by:

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

where C_0 and C_e (mg/L) are the concentrations of anionic dye at initial and equilibrium, respectively. V (L) is the volume of the solution and W (g) is the weight of adsorbent used.

2. 6. Adsorption Kinetics of Anionic Dyes For the adsorption kinetics measurement of anionic dyes onto adsorbent, 25 ml of dye solution with an initial concentration of 50 mg/L was introduced into the flask and mixed with 0.01 g of PANI/CMK-1. The solution was stirred continuously at 298 K. Samples were taken from the solution by fast filtration at different time intervals. The concentration of methyl orange and methyl red in the residual solution were determined and the amount of adsorption (q_t) was calculated according to Equation (2).

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

where q_t is the amount of adsorption at time t , C_0 the initial concentration of dye in the solution, C_t the concentration of dye in the solution at time t , V the volume of the solution, and m the mass of PANI/CMK-1.

3. RESULT AND DISCUSSION

3. 1. Physical and Chemical Properties of the Adsorbents

The quality of the mesoporous carbon and modified mesoporous carbon prepared in this study was examined by Nitrogen adsorption-desorption analysis, X-ray diffraction (XRD) techniques and SEM image. Nitrogen physisorption is the method of choice

to gain knowledge about mesoporous materials. This method gives information on the specific surface area and the pore diameter. Calculating pore diameters of mesoporous materials using the BJH method is common practice.

Figure 2 shows nitrogen adsorption and desorption isotherms measured at 77 K. BET surface areas and the pore size determined by BJH method for the synthesized mesoporous sorbents were determined by the adsorption branches of the isotherms. The two mesoporous materials yield a type IV isotherm. It can be seen that after modification the obtained carbons still have type IV isotherms, indicating that mesoporosity is still preserved.

The narrow pore size distributions centered at about 3.4 nm for CMK-1 and 2.6 nm for PANI/CMK-1 clearly demonstrate that during the preparation of PANI/CMK-1 the removal of silica did not alter the mesopore structure of CMK-1. Table 1 summarizes the important physical properties of mesoporous sorbents.

The lower values of composite compared with pure CMK-1 are mainly ascribed to the presence of dense polyaniline.

In order to check the structural degradation, XRD data of PANI/CMK-1 and CMK-1 recorded in Figure 3 which shows three diffraction peaks that can be indexed to (110), (210), and (220) in the 2θ range from 1° to 10° , representing well-ordered cubic pores [26].

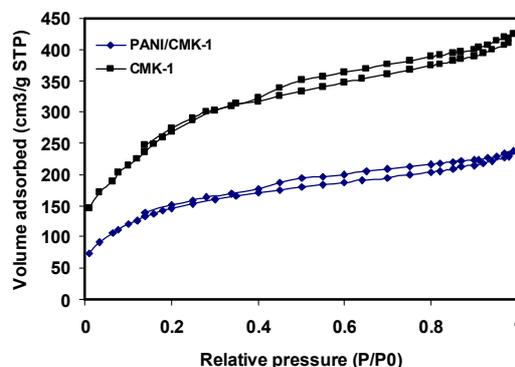


Figure 2. Adsorption–desorption isotherms of nitrogen at 77K on CMK-1 and PANI/CMK-1.

TABLE 1. Textural properties determined from nitrogen adsorption–desorption experiments at 77K

Adsorbent	d spacing (nm)	A_{BET} ($m^2 g^{-1}$)	V_p ($cm^3 g^{-1}$)
CMK-1	3.4	1010.5	0.69
PANI/CMK-1	2.6	769.64	0.54

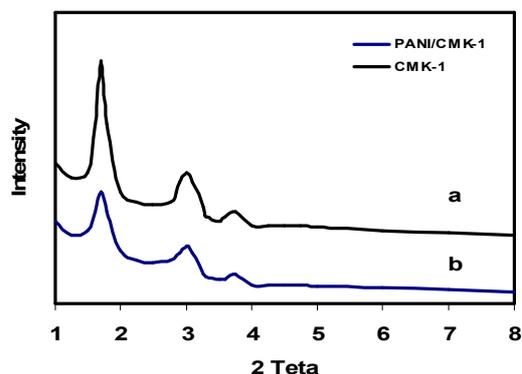


Figure 3. XRD patterns of CMK-1 (a), PANI/CMK-1 (b)

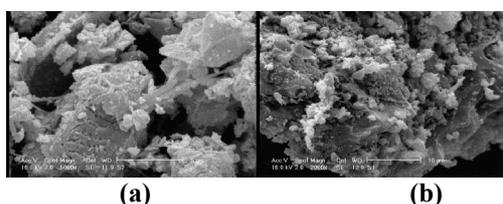


Figure 4. SEM images of CMK-1 (a), PANI/CMK-1 (b)

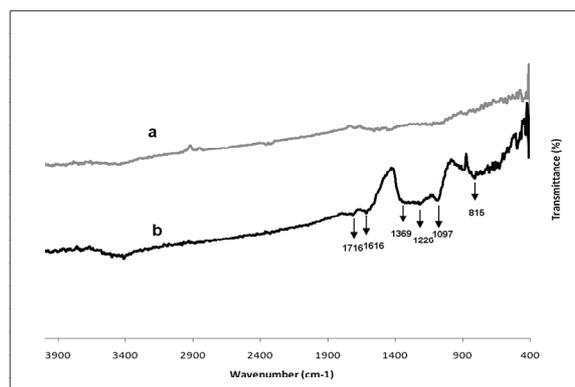


Figure 5. FTIR spectra of CMK-1 (a), composite PANI/CMK-1 (b)

The XRD patterns show well-resolved reflections indicating that CMK-1 nicely maintains its original structure even after the modification. For CMK-1, the cubic structure was well maintained; but, the XRD reflections become less pronounced that might be due to the partial damage of the mesoporous (cubic) structure or due to the decreased contrast between walls and pores due to the cleavage of the carbon species from the pore walls. But the XRD patterns indicate that two samples have highly ordered uniform mesopores.

The morphologies of the obtained pristine CMK-1, PANI/CMK-1 composites were observed by SEM and their images are shown in Figure 4. As seen from Figure 4a, the prepared mesoporous carbon was made of

fasciculi and composite PANI/CMK-1 (see Figure 4b) indicated that the polymerization of aniline occurred either on the surface of the starting material, or inside the pore. And the Scanning electron microscopy showed that the porous carbon particles retained the crystal morphologies for the silica template.

FT-IR spectra of pure CMK-1, PANI/CMK-1 composites are shown in Figure 5. A characteristic stretching vibration of C–O–C group at 1097cm^{-1} appears in FT-IR spectrum 'a' of CMK-1, which would be an important active site for interactions of PANI and CMK-1 in composite. In the spectra of PANI/CMK-1, the key characteristic peaks corresponding to the quinoid ring and the benzene ring are observed at 1716 and 1616 cm^{-1} , respectively. The other peaks at 1369 , 1226 and 815 cm^{-1} can be assigned to the C–N stretching of the secondary aromatic amine, aromatic C–H in-plane bending and out-of plane C–H bending vibration, respectively.

3. 2. Adsorption Studies

3. 2. 1. Effect of Chemical Modification In order to evaluate the efficiency of the prepared adsorbents, the equilibrium adsorption of the anionic dyes was studied as a function of equilibrium concentration. The adsorption isotherms of methyl orange and methyl red on PANI/CMK-1 and CMK-1 are shown in Figures 6 and 7. It is seen that the order of adsorption in terms of the amount adsorbed (mg/g) at different conditions is: PANI/CMK-1 > CMK-1. PANI/CMK-1 registers higher adsorption capacity (75 and 71 mg/g for MO and MR, respectively) than the untreated mesoporous CMK-1 (37 and 15 mg/g for MO and MR, respectively).

The higher adsorption capacity of modified mesoporous carbon can be explained by several facts. This may be because of the hydrophobicity created by polyaniline group. It is also surmised that the presence of a free electron pair causes more interaction between anionic dyes and adsorbent in PANI/CMK-1. In other words, Anionic dyes are weak acids and there are acid and alkaline interactions among amine groups and anionic dyes.

3. 2. 2. Effect of Contact Time and Concentration

The adsorbate concentration and contact time between adsorbent and adsorbate species play a significant role in the process of removal of pollutants from water and wastewater by adsorption at a particular temperature and pH.

The effect of contact time for the removal of anionic dyes by adsorbent is shown in Figures 8 and 9. The dye was rapidly adsorbed during the first 20–25 min, and then the adsorption rate decreased gradually and reached equilibrium in about 2 h. This is obvious from the fact that a large number of vacant surface sites are

available for the adsorption during the initial stage and with the passage of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid phase and in the bulk liquid phase.

The influence of the initial dye concentration on the elimination of methyl red and methyl orange by PANI/CMK-1 mass was studied at initial concentrations of 10– 100 mg/L. As can be seen from Figures 8 and 9 the amount of dye eliminated by the adsorbent increased with increasing dye concentration.

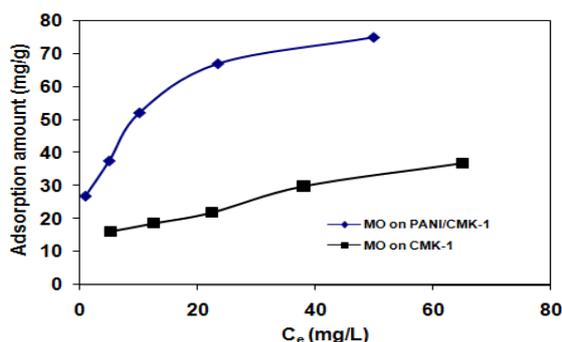


Figure 6. Adsorption isotherm for methyl orange on CMK-1 and PANI/CMK-1 (contact time=2 h, adsorbent dosage = 0.4 g/L)

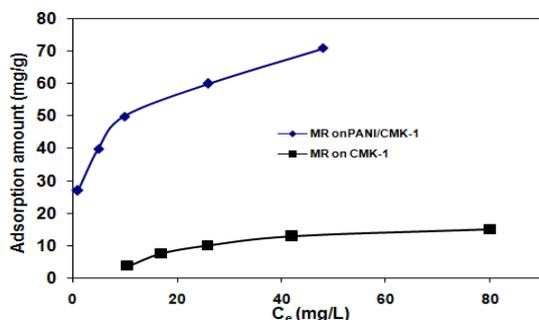


Figure 7. Adsorption isotherm for methyl red on CMK-1 and PANI/CMK-1 (contact time=2 h, adsorbent dosage = 0.4 g/L)

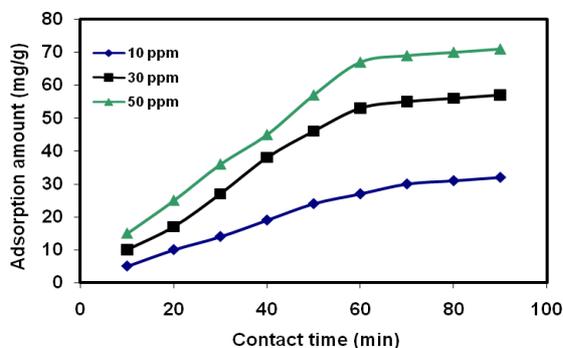


Figure 8. Effect of initial concentration on removal of methyl orange on PANI/CMK-1 (adsorbent dosage = 0.4 g/L).

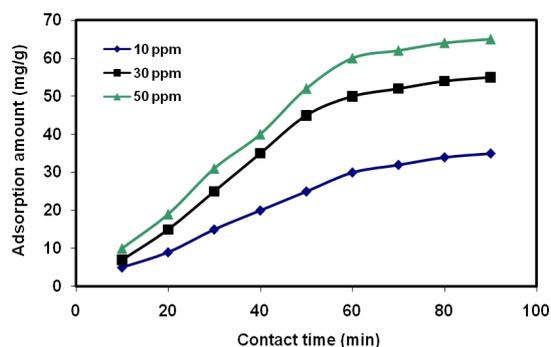


Figure 9. Effect of initial concentration on removal of methyl red on PANI/CMK-1 (adsorbent dosage = 0.4 g/L).

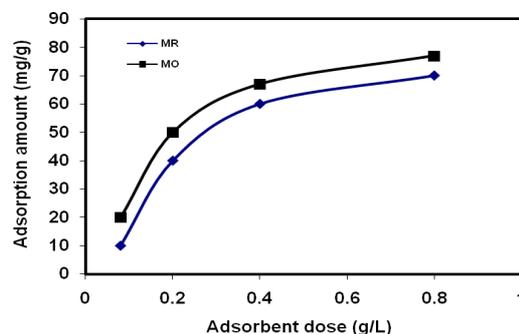


Figure 10. Effect of adsorbent dose on removal of anionic dyes PANI/CMK-1 (Initial concentration = 50 mg/L, contact time = 2h)

3. 2. 3. Effect of Adsorbents Dose The investigation of the mass of adsorbent for dye removal from aqueous solution was carried out using adsorbent masses ranging from 0.001 to 0.02 g, by fixing the initial concentration and volume of dye solutions at 50 mg/L and 25 ml, respectively. The amount of adsorption for dyes was increased with the increase in adsorbent dose. This increase in loading capacity is due to the availability of greater amount of active sites of the adsorbent. The highest amount of dye adsorption was attained for adsorbent masses of at least 0.02 g of adsorbent, as shown in Figure 10. For adsorbent masses higher than these values, the amount of adsorption remained almost constant.

3. 2. 4. Effect of pH The pH value of the solution is an important controlling parameter in the adsorption process. Effect of pH on the removal of anionic dye is shown in Figure 11. The amount of adsorption decreased when the pH increased from 3 to 9 for modified mesoporous carbon. Two possible mechanism of adsorption of dye on the adsorbent may be considered: (a) electrostatic interaction between the adsorbent and the dye molecule, (b) a chemical reaction between the dye and the adsorbent. At pH 3 the H^+ ion

concentration in the system increased and the surface of the mesoporous carbons acquires positive charge by absorbing H⁺ ions. As the carbon surface is positively charged at low pH a significantly high electrostatic attraction exists between the positively charged surface of the carbons and anionic dye, an anionic dye molecule, leading to maximum dye adsorption. As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. Negatively charged surface sites on the pomegranate peel carbons do not favor the adsorption of dye anions due to the electrostatic repulsion. Also lower adsorption of anionic dye at alkaline pH is due to the presence of excess OH⁻ ions, which destabilize anionic dyes and compete with the dye anions for the adsorption sites. The most effective pH was 5 and it was used in further studies.

3. 3. Adsorption Isotherms The equilibrium adsorption isotherm is important in the design of adsorption systems. Three important isotherms are selected in this study, the Langmuir, Freundlich and temkin isotherms (Figures 12-14). The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful application for many sorption processes of monolayer adsorption. The Langmuir equation was applied for the adsorption equilibrium as follows [27]:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \tag{3}$$

where q_e is the amount of the adsorbed dye under equilibrium (mg/g), C_e is the equilibrium concentration of the dye in solution (mg/L), q_m is the monolayer adsorption capacity (mg/g) and K (L/mg) is the constant related to the free energy of adsorption.

The Freundlich isotherm is the earliest known relationship describing the adsorption equation. This fairly satisfactory empirical isotherm can be used for nonideal adsorption that involves heterogeneous surface energy systems [28]. The Freundlich isotherm is commonly given by:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \tag{4}$$

where K_F is a Freundlich constant that shows both the adsorption capacity of an adsorbent and strong relationship between adsorbate and adsorbent. The slope $1/n$, ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. In general, as K_F increases the adsorption capacity of an adsorbent for a given adsorbate increases. K_F and $(1/n)$ can be determined from the linear plot of $\ln q_e$ vs. $\ln C_e$.

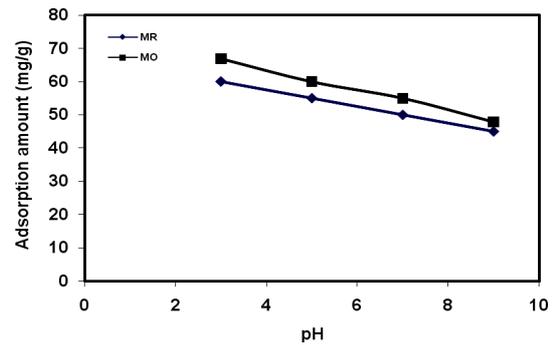


Figure 11. Effect of pH on removal of anionic dye on PANI/CMK-1 (initial concentration = 50 mg/L, adsorbent dose 0.4 g/L, contact time = 2 h).

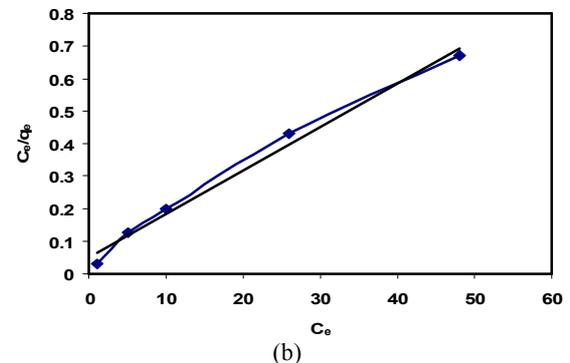
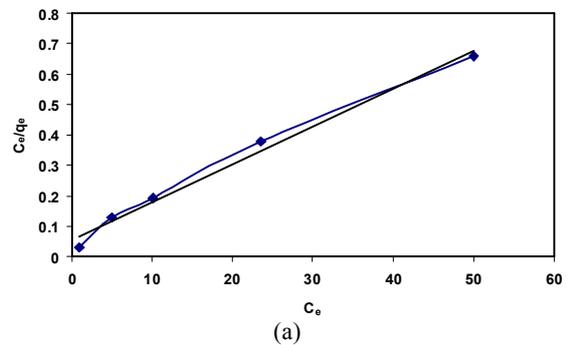
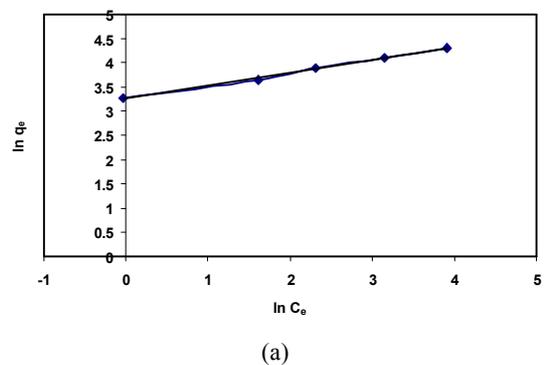


Figure 12. Langmuir Isotherm for adsorption of (a) MO (b) MR on PANI/CMK-1 adsorbent



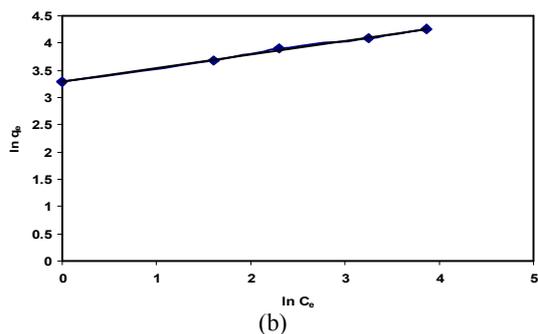


Figure 13. Freundlich Isotherm for adsorption of (a) MO (b) MR on PANI/CMK-1 adsorbent

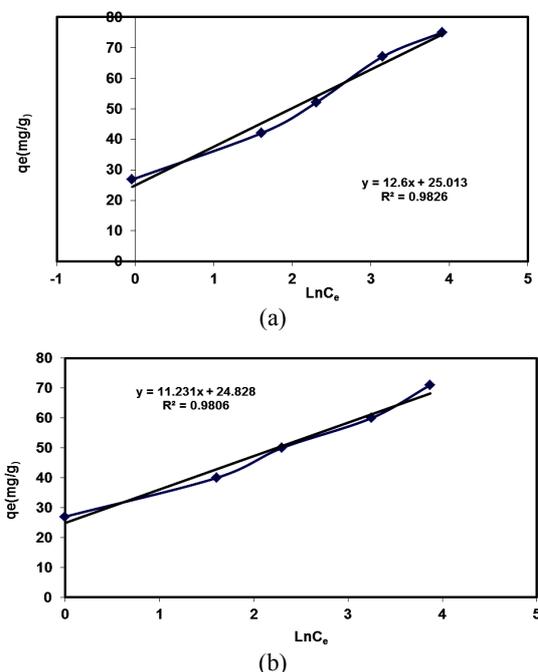


Figure 14. Temkin Isotherm for adsorption of (a) MO (b) MR on PANI/CMK-1 adsorbent

TABLE 2. Langmuir, Freundlich and temkin constants for adsorption of anionic dyes on CMK-1/PANI

Langmuir			
Dye	qm (mg/g)	b (l/mg)	R ²
MO	80	0.23	0.98
MR	75.18	0.26	0.98
Freundlich			
Dye	K _f (mg/g(L/mg) ^{1/n})	n	R ²
MO	26.26	3.78	0.994
MR	27.02	4	0.996
Temkin			
Dye	Ln K _T	B	R ²
MO	1.985	12.6	0.9826
MR	2.210	11231	0.9806

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy. The Temkin isotherm is represented by the following equation:

$$q_e = \frac{RT}{b} \ln (K_T C_e) \tag{5}$$

Equation (5) can be expressed in its linear form as:

$$q_e = B_T \ln K_T + B \ln C_e \tag{6}$$

where, T is the absolute temperature (K), R the universal gas constant (8.314 J/mol.K), K_T the equilibrium binding constant (L/mg), and b the variation of adsorption energy (kJ/mol). B_T is Temkin constant related to the heat of adsorption kJ/mol. The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for adsorbents.

The fitting results, i.e. isotherm parameters and the coefficients of determination, R², are shown in Table 2. It can be seen that Freundlich isotherm fits the data better than Langmuir isotherm. The modified mesoporous carbon adsorbent used in this work has a relatively large adsorption capacity. This indicates that PANI/CMK-1 is effective in removing MO and MR from aqueous solutions.

3. 4. Kinetic Modeling Adsorption kinetics is one of the most important parameters for the evaluation of adsorption efficiency. Two main kinetic models namely the pseudo-first order [29, 30] and pseudo-second order [31, 32] were used in this study to characterize adsorption kinetics.

3. 4. 1. Pseudo First-order and Second-order The pseudo first-order equation is expressed as:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \tag{7}$$

where q_e and q_t are amounts of dye adsorbed (mg/g) at equilibrium and time t (min), respectively, and k₁ is the rate constant of pseudo first-order adsorption (min⁻¹). The values of log (q_e-q_t) were calculated from the kinetic data of Figure 15. The k₁ values and q_e were calculated from slope and intercept from the plots of log (q_e-q_t) versus t for different concentration. The k₁ values, q_e calculated and correlation coefficient is given in Table 3. Also, the calculated q_e values agree with the experimental data (q_{e,exp}). These indicate that the adsorption perfectly complies with Pseudo first-order reaction.

The pseudo second-order kinetic model is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \tag{8}$$

where k_2 is the rate constant of pseudo second-order adsorption (g/mg min). The plots of (t/q_t) versus t for the pseudo second-order model given in Equation (8) were drawn at different solution in Figure 16. The q_e and k_2 values were calculated from slope and intercept of this plots, respectively. The $q_{e,exp}$ values do not agree with calculated ones, obtained from the plots. This results show that the adsorption of anionic dye onto modified mesoporous carbon is not a pseudo second-order reaction.

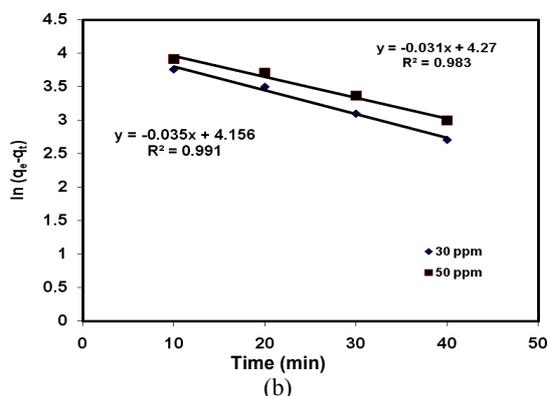
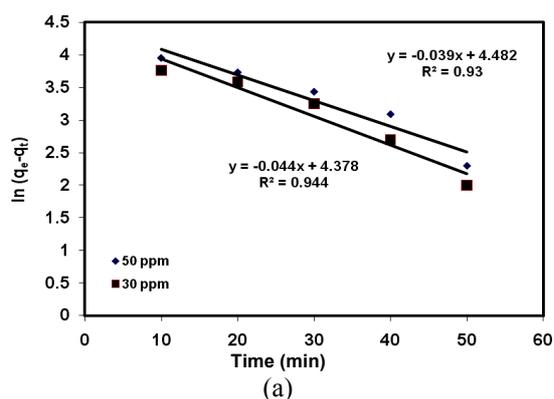


Figure 15. Pseudo-first order kinetics plots for the removal of (a) MO (b) MR on PANI/CMK-1 adsorbent

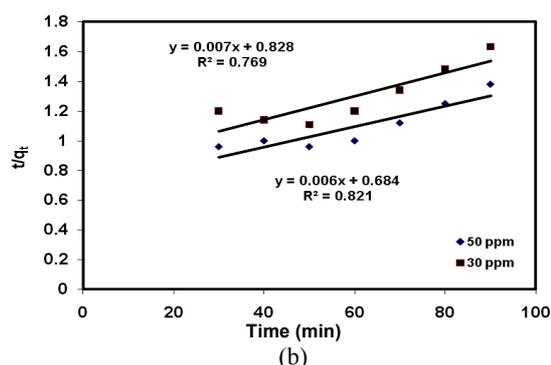
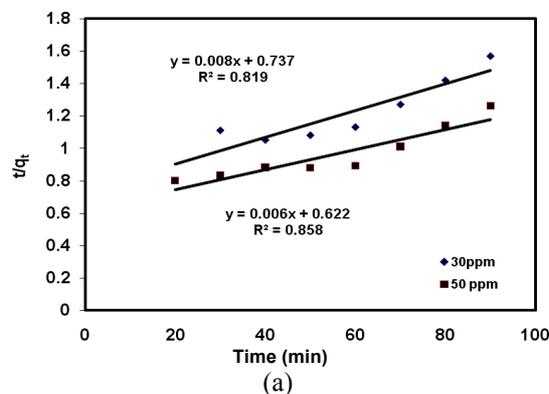


Figure 16. Pseudo-second order kinetics plots for the removal of (a) MO (b) MR on PANI/CMK-1 adsorbent

TABLE 3. Pseudo-first order and Pseudo-second order constants for the removal of anionic dyes by modified mesoporous carbon adsorbent

Dye	Pseudo-first Kinetic		
	q_e (mg/g)	K_1 (L/min)	R^2
MO	88.23	0.039	0.94
MR	63.81	0.031	0.99
Dye	Pseudo-second Order Kinetic		
	q_e (mg/g)	K_2 (g/mg.min)	R^2
MO	161.29	6.18×10^{-5}	0.85
MR	126.58	7.53×10^{-5}	0.82

Table 3 shows that the correlation coefficients of first-order kinetic model are greater than that of the second order kinetic. This fact suggests that the rate of sorption for anionic dyes is dependent on the concentration of the sorbate in the bulk solution rather than the availability of the sorption sites.

4. CONCLUSIONS

The main purpose of this work is the investigation of removal of the anionic dyes (methyl orange and methyl red) from aqueous solutions using mesoporous carbon modified by polymer. For this purpose, nanocomposite PANI/CMK-1 has been prepared obtained by mesoporous carbon and used as new adsorbents for the removal of anionic dyes from aqueous solution. The structural order and textural properties of all the materials are characterized by XRD, SEM and nitrogen adsorption. The characteristic results indicated that the modification was successful and the pore structure of CMK-1 was almost not changed. The maximum adsorption capacity of anionic dyes for PANI/CMK-1 material is higher than that for CMK-1. This may be due

to the hydrophobicity created by amine group, and acid and alkaline interactions among amine group and anionic group. The isotherm data were fitted with Freundlich isotherm.

5. REFERENCES

- Brown, D., "Effects of colorants in the aquatic environment", *Ecotoxicology and Environmental Safety*, Vol. 13, (1987), 139–147.
- Ramakrishna, K.R. and Viraraghavan, T., "Dye removal using low cost adsorbent", *Water Science Technology*, Vol. 36, (1997), 189–196.
- Bozdogan, A. and Goknil, H., "The removal of the color of textile dyes in wastewater by the use of recycled coagulant", *MU Fen. Billimeri. Dergisi Sayi*, Vol. 4, (1987), 83-90.
- Majewska-Nowak, K., "Effect of flow conditions on ultrafiltration efficiency of dye solutions and textile effluents", *Desalination*, Vol. 71, (1989), 127-135.
- Shendrik, O.R., "Electro membrane removal of organic dyes from wastewaters", *Kimiyyi Technology Vody*, Vol. 11, (1989), 467-471.
- Ding, Z., Min, C.W. and Hui, W.Q., "A study on the use of bipolar particles-electrode in the decolorization of dying effluents and its principle", *Water Science Technology*, Vol. 19, (1987), 39-44.
- Anbia, M. and Moradi, S.E., "Adsorption of naphthalene derived compound from water by chemically oxidized mesoporous carbon", *Chemical Engineering Journal*, Vol. 148, (2009), 452-458.
- Anbia, M. and Moradi, S.E., "Removal of naphthalene from petrochemical wastewater streams using carbon nanoporous adsorbent", *Applied Surface Science*, Vol. 255, (2009), 5041–5047.
- Anbia, M. and Mohammadi, K., "An Effective Method for the Removal of ichromate Ion and Furfural from Aqueous Solutions Using a Nanoporous Adsorbent", *Asian Journal of Chemistry*, Vol. 21, (2009), 3347-3354.
- Anbia, M. and Mohammadi, K., "Removal of Copper-Phthalocyanine from Aqueous Solution by Cationically Templated MCM-41 & MCM-48 Nanoporous Adsorbents", *Chinese Journal of chemistry*, Vol. 26, (2008), 2051-2055.
- Anbia, M., Rofouei, M.K. and Husain, S.W., "Mesoporous Lanthanum Tungstate as a Novel Sorbent for Removal of Heavy Metal Ions from Aqueous Media", *Asian Journal of Chemistry*, Vol. 19, (2007), 3862-3868.
- Cooper, P., "Color in Dye House Effluent", Society of Dyers and Colorists, Alden Press, Oxford. 1995.
- Crini, G., "Non-conventional low-cost adsorbents for dye removal: a review", *Bioresour Technology*, Vol. 97, (2006), 1061–1085.
- Fierro, V., Torne-Fernandez, V. and Celzard, A., "Kraft lignin as a precursor for microporous activated carbons prepared by impregnation with *ortho*-phosphoric acid: synthesis and textural characterization", *Microporous Mesoporous Material*, Vol. 92, (2006), 243–250.
- Tseng, R.L. and Tseng, S.K. "Pore structure and adsorption performance of the KOH activated carbons prepared from corncob", *Journal of Colloid Interface Science*, Vol. 287, (2005), 428–437.
- Mizuho, H., Naohito, K., Takeo, N., Matsumoto, K., Kabayama, M., Tamura, T. and Tanada, S., "Adsorption of dyes onto carbonaceous materials produced from coffee grounds by microwave treatment", *Journal of Colloid Interface Science*, Vol. 254, (2002), 17–22.
- Wang, S.B., Zhu, Z.H., Coomes, A., Lu, G.Q. and Haghseresht, F., "The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater", *Journal of Colloid Interface Science*, Vol. 284, (2005), 440–446.
- Anbia, M., Rofouei, M.K. and Husain, S.W., "Synthesis of Mesoporous Lanthanum Phosphate and Its Use as a Novel Sorbent", *Chinese Journal of chemistry*, Vol. 24, (2006), 1026-1030.
- Anbia, M. and Ghaffari, A., "Removal of Malachite Green from Dye Wastewater Using Mesoporous Carbon adsorbent", *Journal of Iranian Chemical Society*, Vol. 8, (2011), 67-76.
- Anbia, M. and Lashkari, M., "Synthesis of amino-modified ordered mesoporous silica as a new nano sorbent for the removal of chlorophenols from aqueous media", *Chemical Engineering Journal*, Vol. 150, (2009), 555-560.
- Anbia, M. and Asl Hariri, S., "Removal of methylene blue from aqueous solution using nanoporous SBA-3", *Desalination*, Vol. 261, (2010), 61–66.
- Mohammadi, N., Khani, H., Gupta, V.K., Amereh, E. and Agarwal, S., "Adsorption process of methyl orange dye onto mesoporous carbon material-kinetic and thermodynamic studies", *Journal of colloid and interface science*, Vol. 362, No. 2, (2011), 457-462.
- Xiaoping, D., Jie, F., Xingxing, X. and Chen, Ch., "Preparation of hydrophilic mesoporous carbon and its application in dye adsorption", *Materials Letters*, 65, (2011), 2486-2488.
- Shao, Y., Wang, L., Zhang, J. and Anpo, M., "Synthesis of hydrothermally stable and long range ordered Ce-MCM-48 and Fe-MCM-48 materials", *Microporous Mesoporous Material*, Vol. 109, (2005), 20835–20841.
- Ryoo, R., Joo, S.H. and Jun, S., "Synthesis of highly ordered carbon molecular sieves via template-mediated structural transformation", *Journal of Physical Chemistry*, Vol. 103, (1999), 7743–7746.
- Jun, S., Joo, S.H., Ryoo, R., Kruk, M., Jaroniec, M., Liu, Z., Ohsuna, T. and Terasaki, O., "Synthesis of new nanoporous carbon with hexagonally ordered mesostructure", *Journal of American Chemical Society*, Vol. 122, (2000), 10712-10713.
- Langmuir, I., "The constitution and fundamental properties of solids and liquids", *Journal of American Chemical Society*, Vol. 38, (1916), 2221–2295.
- Freundlich, H. M. F., "Over the adsorption in solution", *Journal of Physics and Chemistry*, Vol. 57, (1906), 385–470.
- Robinson, T., Chandran, B. and Nigam, P., "Effect of pretreatments of three waste residues, wheat straw, corncobs and barley husks on dye adsorption", *Bioresour Technology*, Vol. 85, (2002), 119-124.
- Malik, P.K., "Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: A case study of acid yellow 36", *Dyes and Pigments*, Vol. 56, (2003), 239-249.
- Ho, Y.S. and McKay, G., "Sorption of dye from aqueous solution by peat", *Chemical Engineering Journal*, Vol.70, (1998), 115-124.
- Ho, Y.S. and McKay, G., "Rotor dynamic coefficients of a thrust active magnetic bearing considering runner tilts", *Process Biochemistry*, Vol. 34, (1999), 451-461.

Modified Nanoporous Carbon Material for Anionic Dye Removal from Aqueous Solution

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در این مطالعه رفتار جذب رنگ‌دانه‌های آنیونی از محلول آبی بر روی مواد نانو متخلخل کربنی (CMK-1) و اصلاح شده با پلی‌مر (PANI/CMK-1) مورد مطالعه قرار گرفت. در ادامه، تأثیر پارامترهای موثر بر فرایند جذب از قبیل دوز جاذب (۸-۰/۸ گرم بر لیتر)، pH محلول ۳-۱۰، زمان تماس و غلظت اولیه (۱-۱۰ mg/L) با استفاده از فرایند بچ مورد بررسی قرار گرفت. نتایج آزمایشی به دست آمده به وسیله‌ی ایزوترم‌های لانگمیور و فروندلیچ و تمکین مورد تجزیه و تحلیل قرار گرفت و مشخص شد که الگوی جذب بر روی جاذب CMK-1/ANI از مدل جذبی فروندلیچ پیروی می‌کند. نظام ساختاری و خواص بافتی مواد جاذب سنتز شده با روش‌های شناسایی معمول مانند تکنیک جذب-واجذب نیتروژن، پراش اشعه ایکس (XRD) و اسپکتروسکوپی زیرقرمز تبدیل فوریه (FT-IR) و تصاویر میکروسکوپ الکترونی (SEM) بررسی شده و نتایج نشان داد که جاذب نانو متخلخل کربنی اصلاح شده یک جاذب بسیار عالی و مناسب برای حذف رنگ‌دانه‌های آنیونی از محیط آبی فاضلاب می‌باشد.

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