Adsorption of Methyl Orange from Aqueous Solution by Polymer of Intrinsic Microporosity: Isotherms and Kinetics Study

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Summary: In this work the adsorption and kinetics studies of methyl orange (MO) on polymer of intrinsic microporosity (PIM 1) was investigated. The results showed that adsorption of MO increases with temperature, suggesting the endothermic nature of sorption process. The adsorption data was found well fitted to the Langmuir model as compared to Freundlich and Temkin models. The kinetics data was described by first order, second order, pseudo first order, pseudo second order, Elovich equation, film diffusion and particle diffusion models. The kinetic data confirmed that the adsorption of methyl orange on PIM-1 follows particle and film diffusion models along with Lagergren pseudo first order and Elovich equations, indicating the sorption as a mixed diffusional process. The activation energy values for the particle and film diffusion processes were 13.09 k J/mol and 13.12 k J/mol respectively whereas, it was 14.11k J/mol according to pseudo first order equation. The low value of activation energy (less than 42 k J/mol) indicates that the adsorption of MO on PIM-1 is diffusional and physical in nature. The values of thermodynamic parameters ensure that the adsorption was endothermic and non-spontaneous with increase in entropy.

Keywords: Adsorption, Methyl orange, Polymer, Modelling, Thermodynamic parameters.

Introduction

Many industries like textile, paper, food, and leather, printing and plastic are the major users of dyes. Most of the dyes are toxic and are considered as a direct threat to the aquatic life [1]. Different toxic, colored and colorless materials, either organic or inorganic, are being released in environment and causes different diseases. The colored substance not only decreases the light absorption by plants of water but also spoils the color and taste of water. Also most of these coloured substances are highly toxic. Methyl orange (MO) is an organic compound which is commonly used as a dye in textile industries and is also used as indicator in acid base titration [2].

Polymer of intrinsic microporosity (PIM-1) is a member of polymers newly synthesized by using bifunctional hydroxylated aromatic and an activated fluorinated monomers [3]. The microporosity of these polymers is intrinsic to the polymer's molecular structure and is independent of processing of material. The intrinsic microporosity of these polymers is due to highly rigid and contorted molecular structure preventing it from effective packing in solid state. Also these polymers are superior to the conventional microporous materials due to their high free volume and internal surface area. The excellent solubility of these polymers in some organic solvents e.g. chloroform, tetrahydrofuran and m-cresol has also been reported. Some of these polymers can be cast into robust, flexible and thermally stable films and have vast applications in gas or liquid separation [4-6].

Reported conventional physicochemical techniques employed for the removal of dyes from water include ozonation, oxidation, reverse osmosis, membrane separation, adsorption and photochemical degradation. Among these, adsorption is considered as an efficient tool for the removal of toxic substances from waste waters [7-9]. Adsorption on the surface of porous material is considered as an important technique for the removal of colored substance which has been investigated in great details [10-14].

The aim of the present work is the removal of methyl orange form aqueous solution using polymer of intrinsic microporosity. In this work we have selected PIM-1 as this polymer is hydrophobic in nature and has high internal surface area and porosity than the conventional microporous materials like zeolites and activated carbons [15]. These properties enable PIM-1 as an active candidate for the adsorption of toxins from aqueous solution. Further, this polymer has unique applications in the transportation of organic compounds and in gas separation [4].

Experimental

Materials and Method

Methyl orange (MO) was purchased from Merck whereas Polymer of intrinsic microporosity

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(PIM-1) was provided by Riedel de Hein. All the solutions were prepared in deionized water. Dilution method was applied to prepare the desired concentration. Batch technique was used for both adsorption and kinetic studies. The density and the surface area of the PIM-1 used in the present study were 0.944 g/cm^3 and 750 m^2/g respectively.

Adsorption Studies

For the adsorption studies, various concentration of MO was mixed with the fine powder of PIM-1 (0.1g). To ensure complete mixing, the reactants were agitated for 3 hours at the stirring speed of 120 rpm in temperature controlled water shaking bath at 300 K. Afterward, the concentration of each solution was determined by noticing the absorbance at λ_{max} (470 nm) in the spectrophotometer model SSI 1103.

Kinetic Studies

Kinetic study was performed by taking 200 ml of MO solution having concentration 4x10^{-4} M which was shaken with 0.5 g of PIM-1 at definite temperature. To find out the concentration of MO after adsorption, the samples were withdrawn, filtered and subjected for absorbance measurement. The kinetic study was carried out in the temperature range 283-313 K.

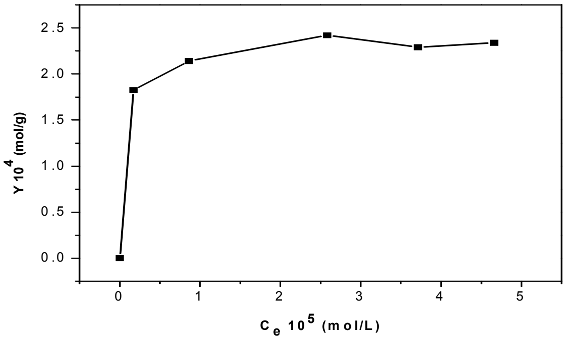

Fig. 1: Adsorption of methyl orange on PIM-1.

Results and Discussion

Adsorption Studies

The adsorption of methyl orange onto PIM-1 was studied at 300 K and adsorption isotherm has been shown in the form of Fig. 1. Various concentration of MO ranging from 1x10^{-5} – 7x10^{-5} M were investigated with fixed amount of PIM-1 (0.1 g). The adsorption isotherm reveals that the uptake of MO was maximum at lowest selected initial concentration. However, the data point shows that equilibrium approaches almost in the lowest selected concentrations of MO showing that the active sites on PIM-1 were readily available to load the maximum amount of methyl orange.

Fig. 2 represents the adsorption data expressed in the form of Langmuir, Freundlich and Temkin models. The validity of MO adsorption on PIM-1 was investigated by applying the Langmuir model which is usually suitable for monolayer adsorption of solute on the surface of adsorbent. This model can be expressed as:

$$C_e/Y = 1/k_b Y_m + C_e/Y_m \quad (1)$$

where, Y_m is the amount of adsorbent required for unimolecular layer formation and k_b is binding energy constant. The plot of Ce/Y against Ce (Fig. 2 (A)) gives a straight line confirming that the adsorption of MO follows Langmuir isotherm model [16]. The validity of this model can also be confirmed from the regression coefficient constant (R^2 = 0.998) which is close to the unity.

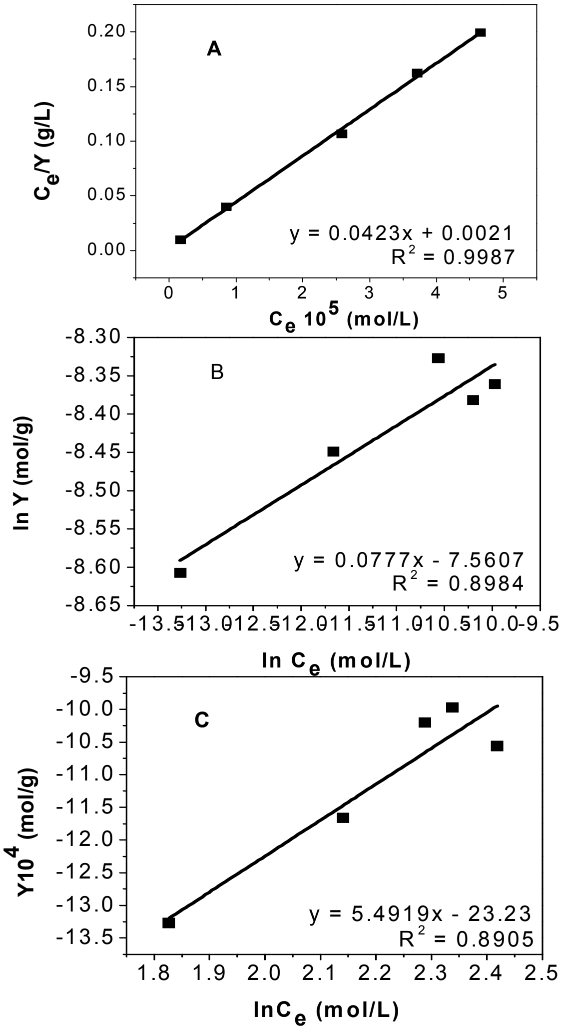

Fig. 2: (A) Langmuir (B) Freundlich and (C) Temkin models for adsorption of MO on PIM-1.

Freundlich model is usually tested for heterogeneous adsorption where the amount of adsorbate on the adsorbent surface increases indefinitely with respect to the solute in aqueous solution. The linearized forms of Freundlich adsorption model is represented by equation 2 whereas the plot according to this model has been represented by Fig. 2 (B).

$$\ln Y = \ln k + (1/n) \ln C_e \qquad (2)$$

where, Y is x/m i.e. amount of adsorbate adsorbed per unit mass of adsorbent, C_e is the equilibrium concentration whereas k and *n* are the physical constants for given system associated to the adsorption capacity and adsorption intensity respectively. The *n* values also give information about the mutual interaction of adsorbed molecules. In present case, the *n* value is greater than unity, suggesting that the forces between the adsorbed MO molecules are repulsive [17].

The Temkin model (Fig. 2 (C)) was also applied to the adsorption data in the form

$$Y = a + b \ln C_e \qquad (3)$$

where, 'a' and 'b' are the constants. From the modelling data, the best fit was found for Langmuir followed by Freundlich and Temkin models, supporting the formation of monomolecular layer of MO on the surface of PIM-1. Similar behavior was observed by Alkan *et al.* for the adsorption of acid blue 62 anionic dyes onto sepiolite [13] and also by Mittal *et al.* for the adsorption of triarylmethane dye on waste material adsorbents [14]. The adsorption parameters extracted from these models are compiled in Table-1.

Table-1: Constants of adsorption derived from Langmuir, Freundlich and Temkin models.

Y_m (Molecules/g)	K_b (dm^3/g)	n (g/dm^3)	a (Mol/g)	b (dm^3/g)
1.42×10^{20}	1.83×10^{6}	12.87	23.23	5.5×10^{4}

Kinetics Studies

From the kinetics data, (Fig. 3) it was observed that time to reach equilibrium decreases with increase in temperature. At 288 K, the adsorption equilibrium was established after 80 minutes, while it decreases to 50 minutes when the study was conducted at 313 K. At higher temperature, the fast adsorption kinetics is due to the frequent collisions of MO particles at the surface of PIM-1 resulting in the establishment of early equilibrium.

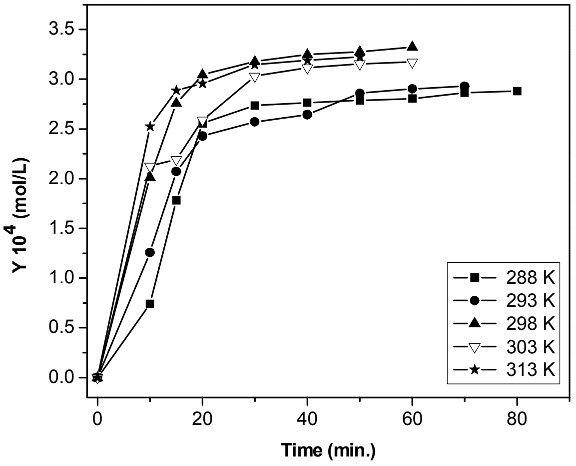

Fig. 3: Adsorption kinetics of methyl orange on PIM-1 at different temperatures.

Different kinetic equations like particle diffusion, film diffusion, Lagergren's pseudo first order and Elovich were applied to the kinetics data of methyl orange on PIM-1. The equation for film diffusion adsorption process is

$$-\ln (1-F) = K_u t \qquad (4)$$

where, F is the fractional attainment which is the ratio of amount adsorbed after time t to the amount adsorbed at equilibrium and K_u is film diffusion rate constant for adsorption. The equations for particle diffusion adsorption process are

$$Bt=6.28318-3.2899F-6.28318(1-1.0470F)^{1/2} \qquad (5)$$

$$B t = - 2.303 \log (1 - F) - 0.49770 \qquad (6)$$

where, B is the rate constant for particle diffusion adsorption process. Equation (5) is used for the value of 'F' from 0 to 0.85 while equation (6) is used when value of 'F' is from 0.86 to 1. Lagergren's pseudo first order and Elovich equations were employed in the form

$$\ln (Y_e - Y) = \ln Y_e - K t \qquad (7)$$
$$Y = a + b \ln t \qquad (8)$$

where, Y_e is amount adsorbed at equilibrium, Y is amount adsorbed at certain time, K is the rate constant while a, b are the constants. The adsorption process followed the particle diffusion, film diffusion, Lagergren equation of pseudo first order and Elovich equation, showing that it was mix diffusional process which follows pseudo first order kinetics [18, 19]. The graphical representation of these equations is given in the form of Figs 4-7. The kinematics of the adsorption data has also been tested for first, second and pseudo second order along with intraparticle diffusion model. However, due to low regression values, these models were found unsuitable. The values of rate constant determined from the models applied in the present study are shown in Table-2.

Table-2: Rate constants derived from film/particle diffusion and Lagergren pseudo first order kinetics at different temperatures.

Temperature (K)	K_u (10^2)	B (10^2)	K (10^2)
283	6.82	6.35	6.82
288	7.57	7.00	6.87
293	8.63	7.94	8.63
303	10.46	9.78	10.46
313	11.46	10.58	11.47

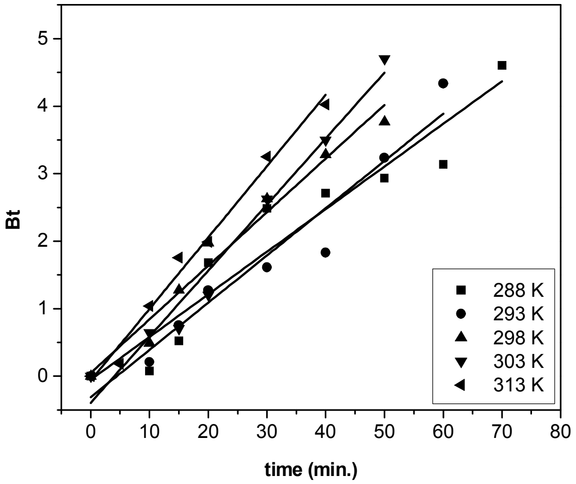

Fig. 4: Particle diffusion model for the adsorption of MO on PIM-1.

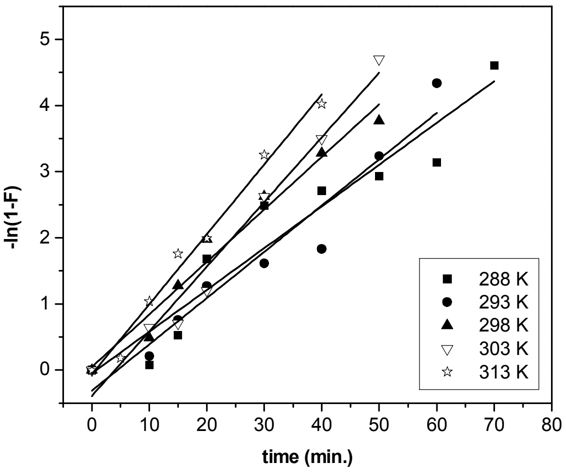

Fig. 5: Film diffusion model for the adsorption of MO on PIM-1.

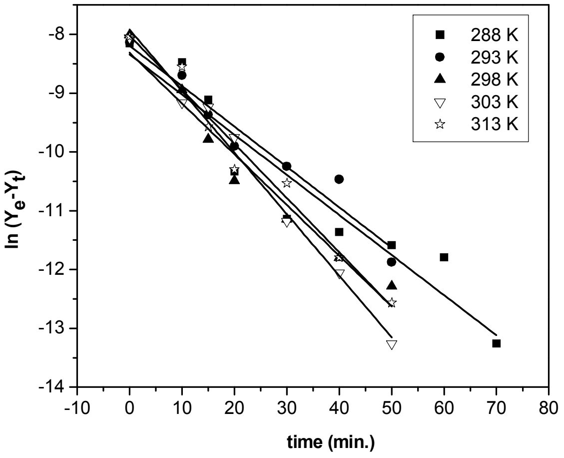

Fig. 6: Lagergren's pseudo first order equation for the adsorption of MO on PIM-1.

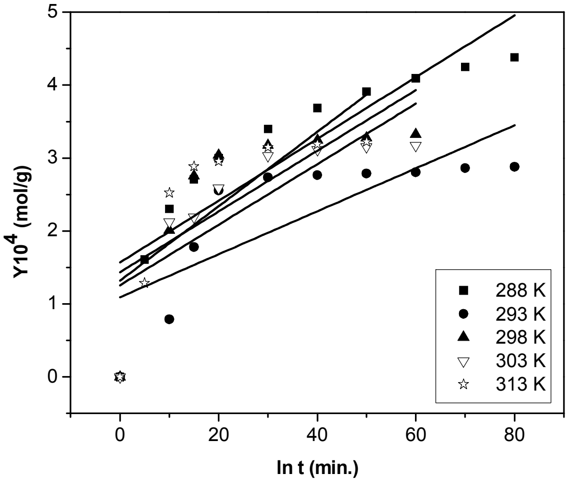

Fig. 7: Elovich equation for the adsorption of MO on PIM-1.

Thermodynamic Parameters

The activation energy was determined by Arrhenius equation which is represented as

$$\ln k = \ln A - E_a/RT \qquad (9)$$

where k is the rate constant, A is the Arrhenius constant, E_a is the activation energy and R is the universal gas constant. The graphical representation of Arrhenius`s equation is shown in Fig. 8. The activation energy of adsorption was found to be 13.09 k J/mol for particle diffusion process, 13.12 k J/mol for film diffusion process and 14.11k J/mol according to pseudo first order equation. The low value of activation energy (less than 42 k J/mol) shows that the adsorption of MO is diffusional controlled and is physical in nature [20]. The positive value of E_a is suggesting that there are some energy barriers as the rate of adsorption increases with the increase in temperature. Thus there is an increased probability of colliding the MO molecules on the surface of PIM-1. The activation energy obtained from the particle diffusional process is closer to the E_a extracted from film diffusional process, which reveals that the predominant mechanism for kinetics of MO is mixed diffusional. Similar types of mechanism have also been proposed in literature [18, 21].

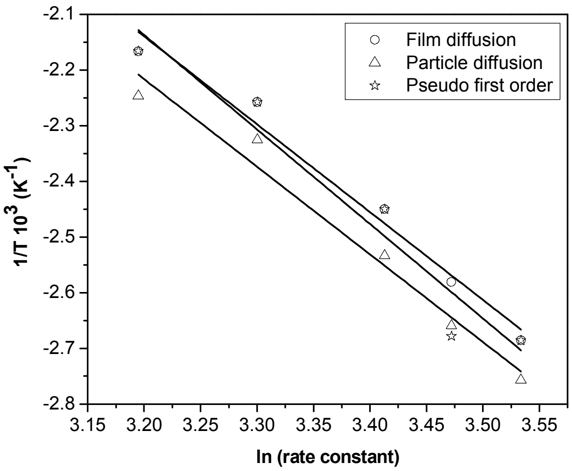

Fig. 8: Arrhenius plot for the adsorption of MO on PIM-1.

Thermodynamic parameters such as ΔH and ΔS were determined by Van`t Hoff`s equation shown in the form

$$K_c = \Delta S/R - \Delta H/R\ T \qquad (10)$$

where, K_c is the equilibrium constant which is determined by the following expression

$$K_c = y_e/C_e \qquad (11)$$

where y_e is the amount of adsorbate adsorbed per unit mass of adsorbate at equilibrium and C_e is the equilibrium concentration of solution of adsorbate. Gibbs free energy (ΔG) for the adsorption process was determined by using well known thermodynamic relation

$$\Delta G = \Delta H - T\ \Delta S \qquad (12)$$

The graphical representation of Van't Hoff equation is shown in Fig. 9 and the values of the thermodynamic constants are given in Table-3. These values show that the adsorption process is endothermic with increased randomness of methyl orange molecules at the interface of PIM-1. The increase in temperature caused a decrease in free energy change showing that the process drives towards spontaneity. Such type of behavior has also been reported by Prado *et al.* for the adsorption of indigo carmine dye on chitin [22].

Table-3: Thermodynamic parameters for the adsorption of MO on PIM 1.

Temperature (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (K/mol)
283	1.355		
288	1.294		
303	1.111	4.81	12.20
313	0.988		

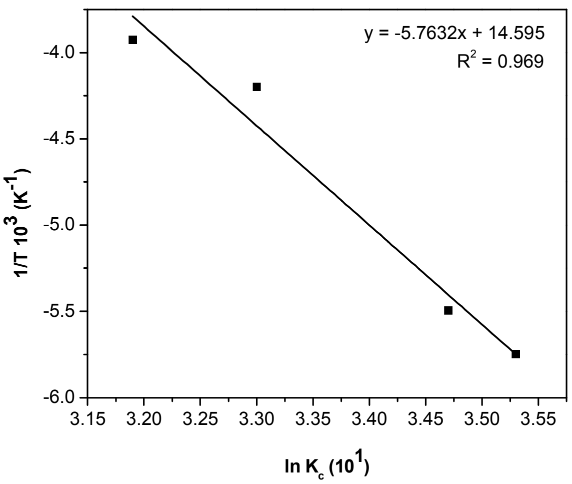

Fig. 9: Van't Hoff's equation for the adsorption of MO on PIM-1.

Conclusions

Adsorption of methyl orange on PIM-1 followed Langmuir adsorption isotherm showing uniform adsorption sites on the surface of adsorbent. The time to reach adsorption equilibrium decreases with the increased in temperature. Adsorption kinetic follows film and particle diffusion equations showing that the process is mixed diffusional in nature driven by pseudo first order. Low activation energy value points towards the physical nature of adsorption process. The positive values of enthalpy, free energy and entropy changes show the process to be endothermic and nonspontaneous with increased randomness on the solid liquid interface.

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