

Study on removal of *m*-phenylenediamine from aqueous solution by adsorption over granular activated carbon

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m-Phenylenediamine (MPD) is used for manufacture of thin film composite reverse osmosis (RO) membrane in polyamide thin film formation by interfacial polymerization. The used *m*-phenylenediamine solution has to be discarded as effluent. Granular activated carbon is found to be an efficient adsorbent for removal of *m*-phenylenediamine from aqueous solution. Brunauer-Emmett-Teller (BET) surface area of the granular activated carbon is 446 m²/g and micropore volume 0.15 cc/g. A systematic study of adsorption of *m*-phenylenediamine over granular activated carbon with different loading of adsorbent in given *m*-phenylenediamine solution concentration and different concentration of *m*-phenylenediamine solution in given adsorbent quantity has been carried out. Adsorption isotherms have been developed in each case. It is found that at 28% w/v concentration of adsorbent, the total MPD present in the 2% aqueous solution is adsorbed. It is found that adsorption of MPD over granular activated carbon follows Freundlich isotherm $x/m = k c^{1/n}$, where $k = 0.4576$ and $n = 4$. Moreover, the study involves kinetics of adsorption of *m*-phenylene diamine over granular activated carbon at different temperatures and it is found that the kinetics of MPD adsorption over granular activated carbon follows Elovich Model. The kinetic study indicates that the optimum temperature of adsorption is 40°C as the MPD adsorption efficiency improves from 30 to 40°C and subsequently drops drastically for 45°C. The optimum temperature for adsorption has been found. It is found that granular activated carbon is an efficient adsorbent for removal of *m*-phenylenediamine from aqueous solution.

Keywords: *m*-Phenylenediamine, Granular activated carbon, Adsorption, Kinetics, Hazardous effluent treatment

Meta-phenylenediamine (MPD) is used in interfacial polymerization to make thin polyamide layer in thin film composite (TFC) reverse osmosis (RO) membrane manufacturing process. Aqueous solution of *m*-phenylenediamine has to be discarded after the batch of making thin film composite RO membrane making process as it is prone to oxidation. In this way, the process of making thin film composite RO membrane generate aqueous MPD effluents. These effluents are hazardous and need proper treatment before disposal.

The efficient way of removing MPD from water is adsorption over granular activated carbon. *Meta*-phenylenediamine has good affinity with the adsorbent granular activated carbon and it can be removed from aqueous solution by adsorption.

With rise in population and rise in unscrupulous sources of water, the use of granular activated carbon (GAC) for removal of organics from water is becoming widespread. Granular activated carbon finds its application in trace contaminant removal, natural organic matter removal, colour and odour removal¹.

Granular activated carbon has been traditionally considered as one of the most versatile adsorbents for removal of organic matter from aqueous solutions². Granular activated carbon has also been successfully used for removal of trace organic contaminants from water³. It has also been reported that surface of activated carbon can be modified by nitric acid, hydrogen peroxide and ammonium peroxydisulfate⁴. Granular activated carbons are used in the form of a carbon bed, usually within a column, for water treatment. The water flows through the bed, where organic molecules present as contaminants are adsorbed on to the carbon surface⁵. Removal of dissolved organic carbon by granular activated carbon in wastewater treatment has been reported⁶.

The adsorption of recalcitrant fluoroaromatic compound by granular activated carbon has also been reported⁷. Granular activated carbon have also been evaluated for the removal of 2-methylisoborneol (MIB)⁸. Removal of MIB and Geosmin using granular activated carbon with or without MIEX pre-treatment

has been reported⁹. Adsorption of chlorophenols over granular activated carbon and bioregeneration of the same has been attempted^{10,11}. Adsorption of quinoline on granular activated carbon (GAC) and bagasse fly ash (BFA) have been studied in a batch system¹². Application of granular activated carbon to adsorb phenol and using microwave (MW) energy to treat the phenol adsorbed by GAC has been attempted¹³. The adsorption potential of bamboo waste based granular activated carbon (BGAC) to remove reactive azo dye from aqueous solution has been investigated using fixed-bed adsorption column¹⁴. The kinetics of pentachlorophenol (PCP) adsorption/desorption with granular activated carbon has been studied¹⁵. Sorption characteristics of toluene on a granular activated carbon (GAC) derived from coconut shell have been investigated at 4 and 20°C¹⁶.

Kinetic and equilibrium studies on the removal of acid dyes from aqueous solutions by adsorption onto activated carbon cloth have been reported¹⁷. Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk has also been done¹⁸. Adsorption of reactive dye on carbon nanotube has been reported¹⁹.

The adsorbents used for dye adsorption and their governing isotherm have been listed in Table 1²⁰⁻³¹.

In this way, a wide spectrum of organics can be removed by granular activated carbon. To the best of authors' knowledge, reports on MPD adsorption over granular activated carbon are not available in literature and thus the study of MPD adsorption over granular activated carbon is a research gap, which has been addressed in the present paper.

Experimental Section

Materials

Technical Meta phenylene diamine (Sigma Aldrich Co. USA), Granular activated carbon (1.5 mm granules, LR grade)

Methods

Nitrogen adsorption on GAC at liquid nitrogen temperature (~77°K) was carried out using ASAP2010 (Micromeritics USA) for the evaluation of specific surface area and pore properties of the sample. Sample was degassed under vacuum (<5 m Hg) at 150°C for 2 h before analysis. Infrared spectroscopic analysis of the GAC was recorded using KBr pellets on Perkin-Elmer, GX FT-IR spectrometer.

Varying Adsorbent quantity for fixed MPD concentration

MPD solution (2%) was prepared by dissolving 20 g MPD in 1 liter water. The prepared solution was distributed equally in 10 conical flasks i.e. 100 mL in each flask. 1, 4, 7, 10, 13, 16, 19, 22, 25 and 28 g of GAC respectively was inserted in each flask. Thus the uniform MPD solution was exposed to different quantities of adsorbents. The conical flasks were kept under stirring for 18 h at 30°C temperature. The collected solutions were filtered with 40 micron Whatman filter paper. Concentration of MPD before and after adsorption equilibrium was measured spectrophotometrically after appropriate dilution of the solutions. UV-visible absorbance of MPD solutions were measured at $\lambda_{max} = 289$ nm using UV-visible spectrophotometer UV 2550 (Shimadzu), equipped with a quartz cell having a path length of 1 cm. The amount of MPD adsorbed

Table 1—Adsorption of different dye composites

Adsorbent	Adsorbate	Isotherm	Reference
Green algae <i>Chlorella Vulgaris</i>	Remazol black	Langmuir	20
Modified barley straw	Acid blue	Langmuir	21
Activated clay	Methyl orange	Langmuir	22
Raw and treated pine cone	Methylene blue	Langmuir and Freundlich	23
Activated pine cone	Congo red	Freundlich	24
Pine cone	Methylene blue	Langmuir	25
Pine leaves	Basic red 46	Langmuir	26
Pine leaves	Methylene blue	Langmuir and Freundlich	27
Chitosan	Reactive blue 19q	Redlich-Peterson	28
Chitosan	Methylene blue	Freundlich	29
Poplar leaf	Methylene blue	Langmuir	30
Chitosan	Congo red	Langmuir	31

onto adsorbent (g g^{-1}), was calculated as given in Eq. (1).

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad \dots(1)$$

where Q_e is the amount of MPD adsorbed on adsorbent at equilibrium (g g^{-1}), C_0 , the initial MPD concentration in solution (mg L^{-1}), C_e , the MPD concentration in solution at equilibrium (mg L^{-1}), m , the mass of adsorbent used (g) and V , the volume of MPD solution taken for adsorption equilibrium (L).

Varying MPD concentration with fixed adsorbent quantity

MPD solution with 1000, 2000, 3000, 4000, 5000, 6000, 7000, 8000, 9000 and 10000 mg/L concentration were prepared by dissolving 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 g MPD in 1 liter distilled water each. Granular Activated Carbon (0.5 g) was inserted in each flask after activating the same by heating in oven at 150°C for 1.5 h. All flasks were kept under uniform stirring at constant temperature of 30°C for 18 h. The solutions were filtered with 40 Micron Whatman filter paper and filtrates were diluted 100 times for determining concentration. The same experiment was repeated with adsorbent quantity 0.5, 1, 2, 5 and 10 g .

Kinetics of MPD adsorption with varying temperatures

Meta phenylene diamine (MPD) (1 g) was dissolved in 1 liter distilled water to make 1000 mg/L solution. The solution was divided in 10 equal fractions to make 100 mL of 1000 mg/L MPD solution in each conical flask. Granular activated carbon (GAC) was taken in a Petri plate, spread uniformly and kept in oven at 150°C for 1.5 h. Thus activated GAC was withdrawn and weighed 10 nos. of 1 g samples. Each weighed sample was inserted in each conical flask for exposing it to MPD solution and stirred at uniform temperature with uniform shaking conditions. The conical flasks were withdrawn at fixed time i.e. 5, 10, 20, 25, 30, 35, 40, 50, 60 and 70 h. The collected solutions were filtered with 40 micron Whatman filter paper and the filtrate was diluted 100 times.

Results and Discussions

Characterization of GAC

Surface properties of GAC were evaluated by adsorption of N_2 at liquid N_2 temperature ($\sim 77\text{K}$). Adsorption isotherm of N_2 on GAC is of type

I according to IUPAC classification, which is characteristic of microporous material with relatively lower external surface area³². Results of surface area, total pore volume and micropore volume are summarized in Table 2. Results of Table 2 indicate that more than 70% of volume and surface area is offered by micropores on the basis of total pore volume and BET surface area.

Study of MPD adsorption over granular activated carbon

To study the maximum possible removal of m phenylenediamine adsorption by granular activated carbon, the experiments were carried out with varying concentration of adsorbent in constant MPD solution concentration.

It is explicit from the data in Table 3 that 100% removal of m phenylene diamine was achieved with 28 g adsorbent loading in 100 mL aqueous MPD solution i.e. 28% (w/v) concentration, which is too high and at this high adsorbent concentration, the adsorption becomes limited by diffusion of m -phenylenediamine molecule to active sites of adsorption.

The isotherm for adsorption of m -phenylene diamine over granular activated carbon follows Freundlich isotherm ($x/m = k c^{1/n}$) with k value 0.4576 and n value as 4.

With increasing adsorbent quantity, the mass transfer by adsorption is limited by diffusion of adsorbate to the active sites. To, overcome the effect

Table 2—Important characteristics of adsorbent

1.	BET Surface area (m^2/g)	446
2.	Langmuir Surface area (m^2/g)	590
3.	Total pore volume at $P/P_0 = 0.99$ (cc/g)	0.21
4.	Micropore volume (cc/g) (from t plot)	0.15
5.	Micropore area (m^2/g) (from t plot)	334

Table 3—MPD Adsorption with varying quantity of adsorbents

Weight of adsorbent (g)	Concentration (mg/L) C_e	% Removal of MPD	Mass of MPD adsorbed/mass of adsorbent Q_e
1.00	14580.93	26.61	0.53
4.00	5459.00	72.52	0.36
7.00	1089.37	94.52	0.27
10.00	312.41	98.43	0.20
13.00	112.51	99.43	0.15
16.00	54.15	99.73	0.12
19.00	20.49	99.90	0.10
22.00	13.82	99.93	0.09
25.00	12.44	99.94	0.08
28.00	0.00	100.00	0.07

of diffusion, study of the effect of varying MPD concentration to fixed adsorbent quantity is necessary.

It is important to study the adsorption of MPD by varying the concentration of MPD solution for the fixed adsorbent quantity. To study this effect, the experiments were performed with given quantity of adsorbent and varying concentration of *m*-phenylenediamine. As shown in Fig. 1, the comparison of adsorption isotherms for 0.5, 1, 2, 5 and 10 g adsorbent quantity manifests Freundlich power law equation. It is explicit from the above results that when lower quantity of adsorbent is exposed to high concentration of *m*-phenylenediamine, the efficiency of adsorption improves as manifested by high Q_e value with 0.5 g adsorbent quantity. Adsorption efficiency declines further with increase in adsorbent quantity as relatively fewer molecules of MPD will get exposed to given number of active sites.

Langmuir linear regression can also be applied to the above data as shown in Fig. 2.

The plot of C_e/Γ versus C_e is linear where C_e is equilibrium concentration and Γ is the amount of MPD adsorbed over the adsorbent. The Fig. 2 indicates that the slope and intercept of the line decreases with increase in adsorbent quantity. When low quantity of microporous adsorbent faces relatively higher concentration of adsorbate, relatively larger percent of available active sites get occupied with adsorbate as compared to the active sites in large quantity of adsorbent. This phenomena results in

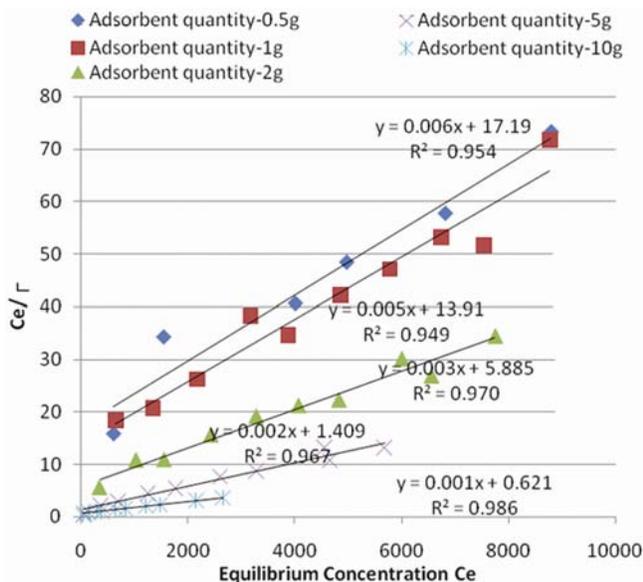


Fig. 1—Comparison of different adsorption isotherms with varying MPD concentrations for different adsorbent quantities

higher Q_e value and larger slope of the line with adsorbent quantity 0.5 g.

Kinetics of MPD adsorption

Study of kinetics of adsorption is important for finding optimum time and temperature of adsorption and design of adsorption systems.

Figure 3 shows quantity of MPD adsorbed is measured and plotted with time. The experiments were carried out at different temperatures i.e. 30, 40 and 45°C. The present study indicates that the optimum temperature of adsorption is 40°C as the MPD adsorption efficiency improves from 30 to 40°C

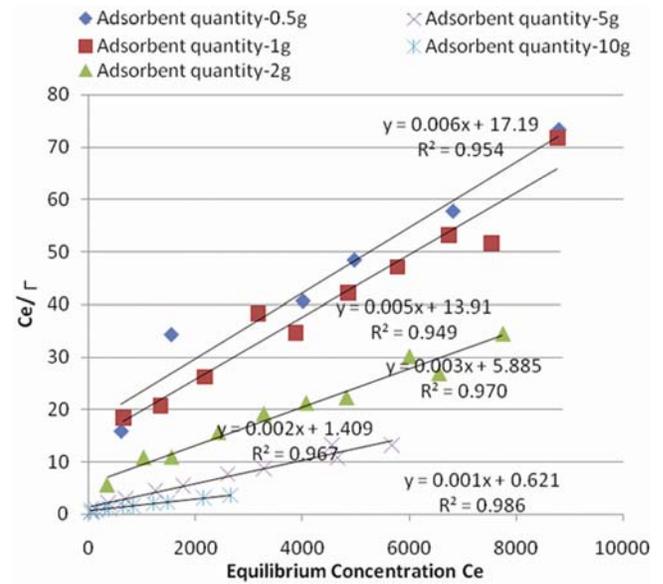


Fig. 2—Langmuir linear regression fit for the adsorption

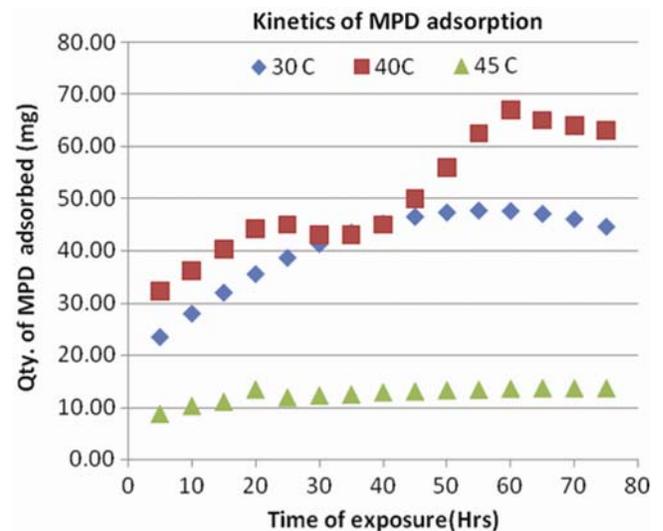


Fig. 3—Kinetics of MPD adsorption

and subsequently drops drastically for 45°C. Moreover, it is observed that isotherm leads to a plateau at about 40 h exposure. There is a fresh rise in MPD adsorption efficiency thereafter and there is another plateau at 65-70 h. This indicates pore diffusion through activated carbon takes time and only happens after certain time which can be seen in Fig. 3 where a fresh rise in MPD adsorption after 45 h is observed. Different models of adsorption have been simulated with the above adsorption data and found that Elovich model suits the best for temperatures 30 and 40°C.

Elovich equation is satisfied in chemical adsorption and is suitable for the systems with heterogeneous adsorption surfaces³³. Characteristics of Elovich model has been reported for dye-chitosan system³⁴. Figure 4 indicates that the Elovich model is the perfect fit for temperature 30 and 40°C. Rise in adsorption efficiency with temperature from 30 to 40°C indicates that certain energy is required to initiate chemical adsorption and further increasing temperature will lead to desorption and therefore not favourable.

Conclusion

Adsorption of *m*-phenylenediamine over granular activated carbon follows Freundlich adsorption isotherm. Upto 100% removal of *m*-phenylenediamine is possible at higher adsorbent loading viz. 28%. The efficiency of adsorption is better when relatively lower quantity of adsorbent is exposed to MPD

solution because of larger number of molecules available for given number of active sites. The Langmuir linear regression fits well for adsorption of *m*-phenylenediamine over granular activated carbon. The kinetics of MPD adsorption over granular activated carbon indicates that the adsorption efficiency is maximum at 40°C with optimum contact time for batch adsorption being 60 h, moreover; kinetics of MPD adsorption suggests that adsorption of MPD over granular activated carbon follows Elovich model with chemical adsorption in which the efficiency of adsorption initially improves with temperature and subsequently declines because of desorption. This clearly demonstrates that with rise in temperature further, adsorbed MPD can be desorbed and the activated carbon can be reactivated for further adsorption. Moreover, the complete process for separation of hazardous MPD can be developed based on this finding.

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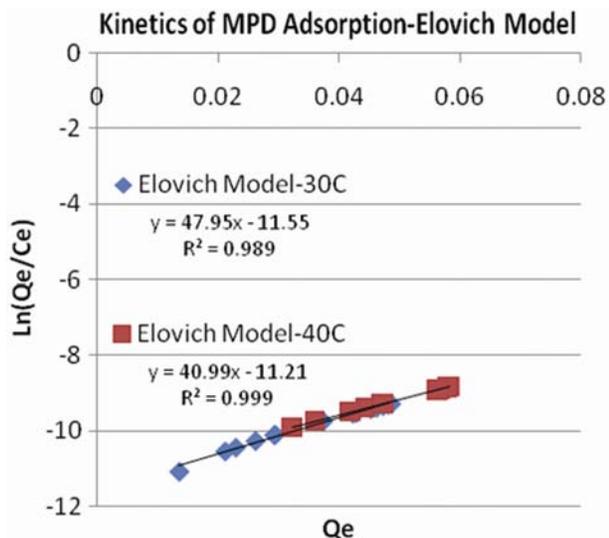


Fig. 4—Elovich model fitting for kinetics of adsorption at temperature 30 and 40°C

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