6

Design and Performance of Fixed Bed Adsorber for Treatment of Malachite Green as Single Solute as Well as in Bisolute Composition

Mitali Sarkar, Mahadeb Das
Department of Chemistry, University of Kalyani
Kalyani-741235, India

Recenzent: Anna M. Anielak
Politechnika Koszalińska

1. Introduction

The effluents from the dye stuff manufacturing and consuming industries that contain a number of contaminants including acid and base, dissolved solids, toxic organic compounds and color are the important source of water pollution. Out of these, color is the first contaminant to be recognised because it is visible to human eye. The dyes present in the effluents may undergo chemical as well as biological changes, consume dissolved oxygen from the stream, disturb the aquatic ecosystem and lower the aesthetic value of water. There are two major technologies for treatment of organic in waste waters i.e. oxidation and adsorption [1, 2]. In oxidation methods UV/ozone or UV/ H_2O_2 treatments are possibly the best technologies to totally eliminate organic carbons in waste water [3], but they are only effective in waste water with very low concentrations of organic compounds. Thus significant dilution is necessary as a facility requirement. In adsorption methods, activated carbon and polymeric resins are the best adsorbent for removal of organic wastes from relatively concentrated waste water [4], but the high cost of adsorbents and difficulty in regeneration make their use limited.

In the search for a low cost adsorbent in our laboratory fly ash, the waste solid generated from thermal power plant, was found to be a potential adsorbent for removal of organic pollutants like dye, surfactant and phenol [5-7] as a single solute. Treatment of single solute using fly ash is relatively simple compared to the real samples which contain more than one solute that are adsorbed simultaneously and competitively on the fly ash. The aim of present study therefore is to propose the mechanism of bisolute adsorption of dye (malachite green) and organic pollutant (phenol) and performance evaluation or the validity of the model in a fixed bed adsorbed. Adsorption isotherms have been used for preliminary selection of an adsorption of an adsorbent to find out the effectiveness of adsorption as well as indication for maximum quantity that can be adsobed by a particular unit. However, adsorption isotherms can not give accurate scale up data in the fixed bed system because (i) adsorption in column is not at equilibrium, (ii) adsorbent rarely becomes totally exhausted in commercial processes, (iii) the effects of recycling remain unknown, and (iv) the isotherms can not predict chemical or biological changes occurring in the adsorbent. Therefore the practical applicability of the adsorbent in column operation has been investigated to obtain a factual design model in the case of single solute as well as in presence of a second solute i.e. the case of bisolute composition.

2. Materials and methods

Fly ash, the solid waste from Bandel thermal power station, West Bengal, India, was collected from the channel approaching the ash pond in ten occassions in a month. It is dried and sieved for different mesh size and the mesh size of 500μm was used for the adsorption of dye (malachite green) and phenol. The average composition of fly ash was described elsewhere [6]. The surface area was determined by BET measurement.

Analytical grade reagents were used for all the experiments. Stock solutions malachite green (18.25mg.dm^{-3}) and phenol (5.0x10^{-2} mg.dm^{-3}) were prepared by dissolving the appropriate amount in double distilled water. Malachite green (EM) was purified by recristallisation from the methanol solutions prior to use and the purity was checked on TLC plate. Fresh stock of phenol (Ranboxy, India) and methanol (Spectrochem, German) were purified by fractional distillation [8,9]. Concentrations of malachite green (MG) and phenol as single solute were determined by measuring the absorbance at 617 nm and 270 nm respectively using Hitachi, UV-VIS spectrophotometer. pH of the solutions were measured by(Systronics, India) pH meter.

Single solute (malachite green, phenol) and bisolute (malachite green+phenol) adsorption studies were performed by shaking 1.0 gm and 2.0 gm respectively of fly ash and 50 ml of aqueous solutions of appropriate solute concentrations and pH in stoppered flasks in an orbital shaker equipped with thermostat (Remi, 12R, India) for two hours. Column experiments were performed in a glass tube (16 cm x 0.06 cm i.d.) with a tap at the bottom. The column was filled with fly ash with gentle agitation following the method of Fornwalt and Hutchins [10]. 5.0 gm of fly ash making a bed length 6.5 cm was used in column experiment. The effluent solution containing single solute (malachite green, phenol) and bisolute (malachite green+phenol) were passed through the column bed at a fixed flow rate 0.8 ml/minute in a down flow manner. The concentration of the eluant was determined through spectrophotometric analysis by measuring the absorbance at 617 nm and 270 nm respectively for malachite green and phenol. Concentrations of malachite green and phenol in bisolute composition were determined [11] solving the following equations (1) and (2).

$$A_{617} = a_1(617).l.c_1 + a_2\,(617).l.C_2 \tag{1}$$

$$A_{270} = a_1(270).l.c_1 + a_2\,(270).l.C_2 \tag{2}$$

where A_{617} and A_{270} are the absorbance at 617 nm and 270 nm respectively when measured experimentally on bi-solute solutions. The parameters a_1 (617) a_2 (617), a_1(270) and a_2(270), are the molar extinction co-efficients of solute 1 (MG) and solute 2 (phenol) measured at 617 nm and 270 nm respectively. C_1 and C_2 are the respective concentrations of solute 1 and solute 2 in bisolute composition and l is the path length.

Desorption of solutes retained on fly ash from the column was performed using methanol as the eluting solvent at a constant flow rate of 0.8 ml/minute. The effluent was collected from the column end and the concentrations of MG and phenol were determined.

3. Results and discussions

In order to achieve the maximum adsorption efficiency batch experiments with single solutes viz. MG and phenol were performed and the optimum conditions for adsorption in each case were established. It was found that for both phenol and malachite green the process is favorable and adsorption percent increased with lower initial concentration, increased dose and lower particle size of fly ash and increased temperature [12, 13]. The equilibrium adsorption data of MG and phenol were studied in the range of pH 2-10.

The extent of adsorption is maximum in pH range 6-8 for phenol and 6.5- 7.5 for MG both for single and bisolute composition. It was observed that MG reaches equilibrium within 70 minutes and 2 hrs for phenol. However, although finer particles 375 μm of fly ash indicated higher adsorption, for practical purposes in order to avoid chocking of column bed particle size of 500 μm was chosen. Moreover, for both the case the process is thermodynamically favorable as indicated by negative free energy change (a measure of spontaneity) and increased entropy (a measure of randomness).

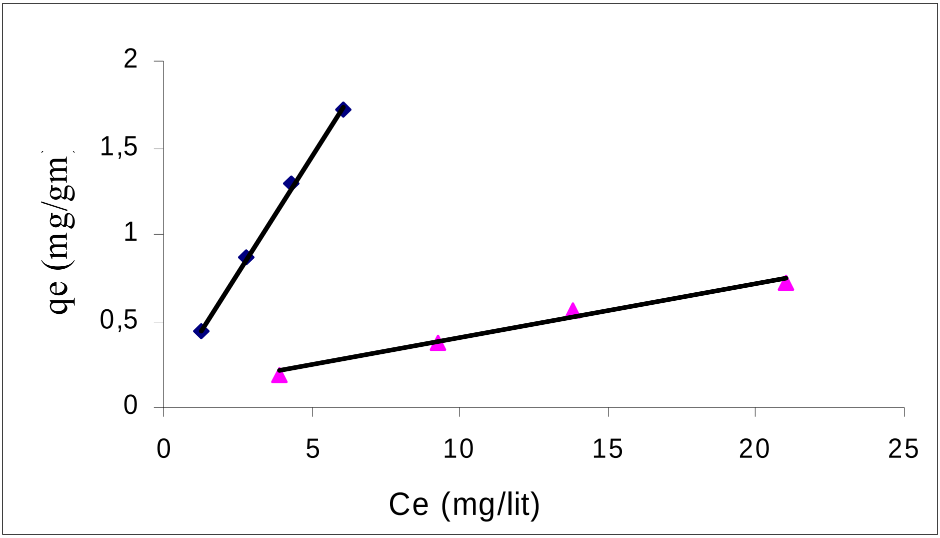

Fig. 1. Plot of Ce vs qe of MG in (i) single solute and (ii) bisolute composition
Rys. 1. Wykres zależności Ce od qe ZM w (i) roztworze jednoskładnikowym i (ii) dwuskładnikowym

The equilibrium adsorption data of malachite green as single solute and in presence of phenol were presented graphically in fig 1. It is observed that in the domain of the concentration range studied the amount of solute adsorbed increased with increase in the initial concentration of the single solute. The extent of adsorption of malachite green is lowered in presence of phenol. Adsorption data were tested with both for Langmuir and Freundlich isotherm model with following expression.

Langmuir isotherm - $C_e/q_e = 1/Q.b + C_e/ Q$ (3)

Freundlich isotherm - $\log q_e = \log K + 1/n \log C_e$ (4)

Where:

$q_=$ denotes amount adsorbed per gm of fly ash at equilibrium
$C_{e\,=}$ concentration remain in at equilibrium
Q, b are Langmuir constants and K, n are Freundlich constant.

The adsorption isotherm parameters were evaluated using least square procedure and presented in Table 1. The validity of a particular isotherm model was judged using statistical parameters R^2 and SE. Higher R^2 and lower SE indicates the favorable situation. It can therefore be concluded that Langmuir adsorption isotherm model is applicable for single solute composition of both MG and phenol. The parameters obtained from single solute experiments are used to predict the isotherm for bisolute composition using the Langmuir model presented as,

$$q_{1}= Q_{1}.C_{1,e}/\ 1+ (b_{1}C_{1,e}+ b_{2}C_{2.e}) \qquad (5)$$

$C_{1,e}$ and $C_{2,e}$ indicate the equlibrium concentration of solute 1 and 2 respectively.

as well as Freundlich model presented as,

$$C_{1,e} = q_{1}/q_{1}+q_{2}\ [\ 1/K_{1}\ (q_{1} + n_{1}/n_{2.}\ q_{2})\ ]^{1/n}{}_{1} \qquad (6)$$

The experimental values of q_1 and q_2 were compared with the values calculated from Langmuir and Freundlich model and the applicability of isotherm model was predicted in case of bisolute composition (Table 2). The amount of solute adsobed by fly ash at equilibrium in each case was calculated as

$q_{1}= (C_{i}- C_{e}/m).\ V$

where:

Ci is the initial concentration of solute, m is the mass of the fly ash and V is the volume.

Table 1. Isotherm constants and the statistical parameters for single solute adsorption
Tabela 1. Stałe izoterm i parametry statystyczne dla adsorpcji z roztworu jednoskładnikowego

Component	Q	b	R^2	SE	K	I/n	R^2	SE
MG	1.46	2.79	0.9999	0.051	9.616	0.166	0.8412	0.812
Phenol	15.87	0.013	0.9999	0.081	0.9808	0.4205	0.8516	0.782

Analysis of Fig. 1 revealed that the extent of adsorption decreases in presence of second solute. Interestingly, however, the total amount of MG and phenol adsorbed from bisolute system is less than the sum of the solutes adsorbed individually at the same concentration. This may be explained in the light of composition between the solutes for active sites.

Column experiments with single solutes of MG and bi-solute sample were performed and breakthrough capacity was evaluated. Solute mixture are used to obtain. Breakthrough curves were obtained by plotting bed volumes versus effluent concentrations (Fig.2). It is observed that upto a certain volume, the concentration in the effluent is zero, which sharply increases later and finally reaches the influent saturation. The breakthrough capacity which is based upon the total amount adsorbed until the effluent concentration becomes constant are computed for, malachite green as single solute and in presence of phenol. It indicates that breakthrough capacity (BTC) is somewhat higher in single solute case compared to that in presence of phenol. Further the BTC is found lower in each case compared to the total capacity of column bed as evident from the lower value of saturation compared to the influent concentration (corresponding to $A/A_0=1$). It should be noted that as the Lambert Beers law is obeyed in the studied concentration range, the concentration terms are replaced by absorbance. The ultimate concentration value are obtained from the absorbance value. In addition to removal of MG both as single solute and bisolute composition it is recovered that from the fly ash by solvent elution using methanol as eluent.

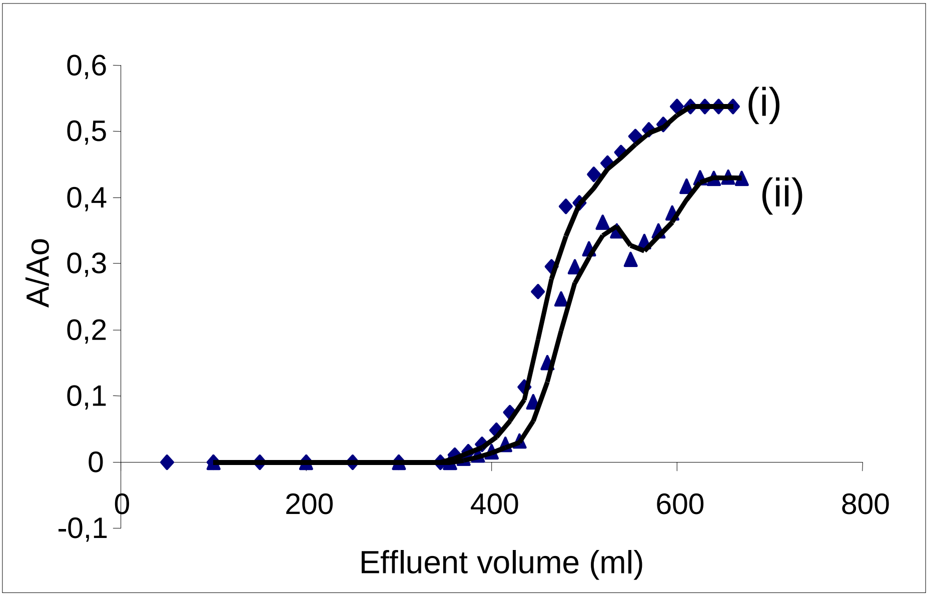

Fig. 2. Breakthrough curve for MG as (i) single solute and (ii) bisolute composition
Rys. 2. Krzywa przełamania dla ZM w roztworze (i) jednoskładnikowym i (ii) dwuskładnikowym

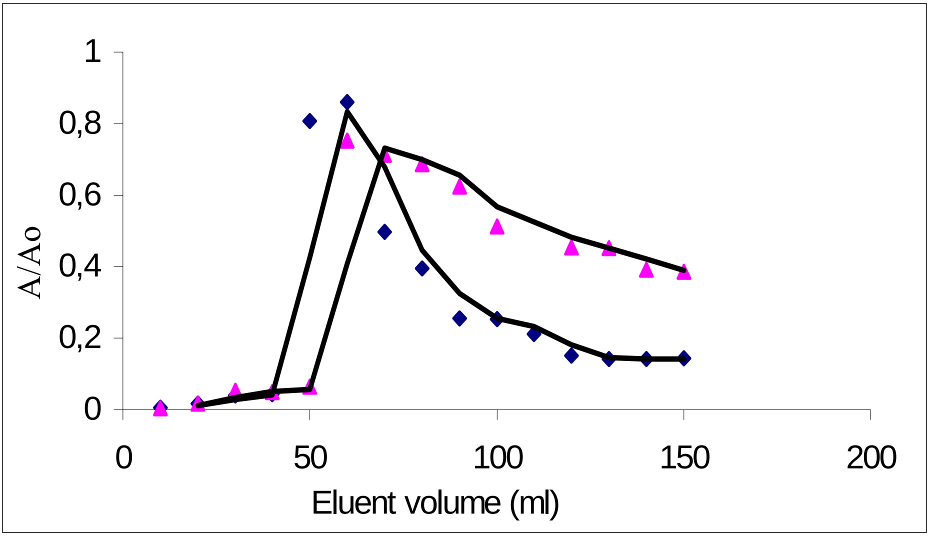

Fig 3. Elution curve of MG as (i) single solute and (ii) bisolute composition

Rys. 3. Krzywa wymywania ZM jako składnika roztworu (i) jednoskładnikowego i (ii) dwuskładnikowego

Table 2. Comparison of experimental bisolute adsorption data with Langmuir and Freundlich isotherm model

Tabela 2. Porównanie eksperymentalnych danych odsorpcji z roztworu dwuskładnikowego z modelem izoterm Langmuira i Freundlicha

Composition	Initial conc. (mg.l^{-1})	q_{exp}	q_{l} (std.dev)	q_{f} (std.dev)
MG in 18.25	9.125	0.1970	0.2920	0.315
	0.3714	0.3840	0.282	
Presence of phenol 150 ppm	27.37	0.5582	0.4854	0.413
	36.50	0.7205	0.5495	0.585

Further, in addition to removal, phenol and MG were recovered from their retained phase using methanol as eluent. The elution curves (Fig. 3) indicate that quantitative elution is effected in case single solute composition than when present together with phenol. It indicates that complete elution requires much eluent in the bisolute situation. The data further indicates that regeneration of fly ash is possible for fresh adsorption. Possibly the solvent elution together with thermal regeneration provides better results for mixed and bisolute composition. It is observed that the same column can be used for 20 cycles of adsorption-elution without reducing the BTC.

References

1. **Anielak A.M.:** *Phenomena Occuring on Phase Boundary in a Process of Coagulation and Co-Precipitation,* Environmental Science Research, Volume 51 - 1996, 179-192, Serie Editor Herbert S. Rosenkranz. University of Pitsburgh 130 De Soto Street. Pennsylvania. Plenum Press – New York and London
2. **Anielak A.M.:** *Post-dying wastewater treatment in co-precipitation and sorption process,* Technical University of Koszalin, 123, 1995
3. **Ruppet G., Bauer R., Heisler.:** *UV-O_3, UV-H_2O_2, UV-TiO_2 and the photo-fenton reaction - comparison of advanced oxidation process for wastewater treatment*, Chemosphere 28,1447-1454, 1994
4. **Blun D.J.W., Suffet I.H., Duguet J.P.:** *Estimating the activated carbon adsorption of organic chemicals in water*, Crit.Rev. Environ. Sci. Tech. 23,121-136, 1993
5. **Sarkar M., Poddar S.:** *Study of the adsorption of methyl violet onto fly ash.*, Anal. proc. including anal. commun., 31, 213-215, 1994
6. **Sarkar M., Acharya P.:** *Equlibrium process optimisation for adsorption of phenol from aqueous solution on fly ash during batch operation*, The Env. Prot. 2, 103-111, 2000
7. **Sarkar M., Das M., Manna S., P Acharya.:** *Utilization of fly ash the solid waste generated from thermal power plant*, Geoenvironmental Reclamation Eds. A.G. Paithankar, P.K. Jha, R.K. Agarwal, Oxford and IBH Publishing Co. Pvt. Ltd., New Delhi 191-194, 2000
8. **Reddick J.A., Bunger W.B., Sakano A.I.:** *Organic solvents*, *Techniques of chemistry,* 4th edition, John Wiley and Sons. New York, 1986
9. **Vogel A.I.:** *A text book of practical organic chemistry*, 5th edition, John Weley and Sons. New York, 1986
10. **Forwalt H.J., Hutchins R.A.:** *Purifying liquids with activated carbon*, Chem. Eng. 73,179-184, 1966
11. **Vogel A.I.:** *A Text Book of Quantitative Inorganic Analysis*, 3rd ELBS, 1964
12. **Sarkar M., Acharya P.:** *Thermodynamic study on the adsorption of phenolic compounds on fly ash, generated from Bandel Thermal Power plant*, The Environmentalist (in press), 2001
13. **Sarkar M., Das M.:** *Modelling the single solute adsorption behavior of Malachite green* (communicated), 2001
14. **Fritz W., Merk W., Schlunder E.U.:** *Competitive adsorption of two dissolved organics onto activated carbon*, Int. Eng. Sci., 36, 731-741, 1981

Projekt i działanie adsorbera ze stałym złożem do usuwania zieleni malachitowej z roztworu jednoskładnikowego jak również dwuskładnikowego

Streszczenie

W poszukiwaniu taniego adsorbentu w naszym laboratorium przekonano się, że popiół lotny – stały odpad powstający w elektrociepłowni – może być potencjalnym adsorbentem do usuwania takich zanieczyszczeń organicznych jak: barwniki, środki powierzchniowo czynne i fenol z roztworów jednoskładnikowych. Usuwanie zanieczyszczenia z roztworu jednoskładnikowego przy użyciu popiołów lotnych jest stosunkowo proste w porównaniu do próbek prawdziwych, zawierających więcej niż jeden składników, które adsorbowane są na popiołak lotny jednocześnie, konkurując ze sobą. Dlatego też celem przedstawionych badań jest zaproponowanie mechanizmu adsorpcji z roztworu dwuskładnikowego barwnika (zieleń malachitowa) i zanieczyszczenia organicznego (fenol) oraz ocena działania lub prawdziwości modelu przy zastosowaniu stałego złoża adsorpcyjnego. Do wstępnej selekcji adsorpcji adsorbentu użyto izoterm adsorpcji, aby zbadać skuteczność adsorpcji a także granicę maksymalnej ilości, która może być zaadsorbowana przez określoną jednostkę. Jednakże izotermy adsorpcji nie mogą oddać dokładnej skali danych uzyskanych na instalacji ze stałym złożem, ponieważ: (i) adsorpcja w kolumnie nie jest w stanie równowagi, (ii) adsorbent rzadko zostaje całkowicie wyczerpany w czasie prowadzenie procesów na skalę przemysłową, (iii) wpływ recyrkulacji pozostaje nie znany, (iv) izotermy nie mogą przewidywać zmian chemicznych lub biologicznych zachodzących na adsorbencie.

W związku z tym zbadano praktyczne zastosowanie adsorbentu w systemie kolumnowym, aby otrzymać faktyczny model w przypadku pracy na roztworze jednoskładnikowym oraz w obecności drugiego składnika tj. przypadek roztworu dwuskładnikowego. Badania wykazały, że adsorpcja zarówno fenolu jak i zieleni malachitowej jest korzystna procent adsorpcji wzrastał wraz ze spadkiem stężenia początkowego, wzrostem dawki, spadkiem rozmiaru ziaren popiołu lotnego oraz wzrostem temperatury. Wykonano badania na systemie kolumnowym z zastosowaniem jednoskładnikowego roztworu zieleni malachitowej oraz próbek dwuskładnikowych i wyznaczono pojemność do punktu przełamania. Wyniki pokazują, że pojemność jest nieco wyższa w przypadku roztworu jednoskładnikowego w porównaniu do roztworu z zawartością fenolu. Kolejne badania wykazały, że możliwa jest regeneracja popiołu lotnego do ponownego użycia w procesie adsorpcji, przy użyciu metanolu jako eluentu. W procesie tym możliwe jest także odzyskiwanie fenolu i zieleni malachitowej. W czasie badań zaobserwowano, że ta sama kolumn może być używana przez 20 cykli adsorpcja-regeneracja bez utraty pojemności adsorpcyjnej.