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

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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/ H₂O₂ 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 adsorbed 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 occasions 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 recrystallisation 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 (mal-
achite 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).

\[ A_{617} = a_1(617).l.c_1 + a_2(617).l.C_2 \]  
\[ A_{270} = a_1(270).l.c_1 + a_2(270).l.C_2 \]

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).
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.

\[
\text{Langmuir isotherm - } \frac{C_e}{q_e} = \frac{1}{Q}.b + \frac{C_e}{Q} \tag{3}
\]

\[
\text{Freundlich isotherm - } \log q_e = \log K + \frac{1}{n} \log C_e \tag{4}
\]

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 ad-

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**Fig. 1.** Plot of \( C_e \) vs \( q_e \) of MG in (i) single solute and (ii) bisolute composition

**Rys. 1.** Wykres zależności \( C_e \) od \( q_e \) ZM w (i) roztworze jednocząsteczkowym i (ii) dwucząsteczkowym
sorption 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,

\[ q_1 = \frac{Q_1 C_{1,e}}{1 + (b_1 C_{1,e} + b_2 C_{2,e})} \]  

(5)

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

as well as Freundlich model presented as,

\[ C_{1,e} = \frac{q_1}{q_1 + q_2} \left[ \frac{1}{K_1 (q_1 + n_1/n_2 q_2)} \right]^{1/n_1} \]  

(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 adsorbed by fly ash at equilibrium in each case was calculated as

\[ q_1 = (C_i - C_e/m) \cdot V \]

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

<table>
<thead>
<tr>
<th>Component</th>
<th>Q</th>
<th>b</th>
<th>R^2</th>
<th>SE</th>
<th>K</th>
<th>I/n</th>
<th>R^2</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>MG</td>
<td>1.46</td>
<td>2.79</td>
<td>0.9999</td>
<td>0.051</td>
<td>9.616</td>
<td>0.166</td>
<td>0.8412</td>
<td>0.812</td>
</tr>
<tr>
<td>Phenol</td>
<td>15.87</td>
<td>0.013</td>
<td>0.9999</td>
<td>0.081</td>
<td>0.9808</td>
<td>0.4205</td>
<td>0.8516</td>
<td>0.782</td>
</tr>
</tbody>
</table>

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 up to 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
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 regenera-
tion 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
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 przekonało 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 popiołach lotnych jednocześnie, konkurując ze sobą. Dlatego też celem przedstawionych badań jest zaproponowanie mechanizmu adsorpcji z roztworu dwuskładnikowego barwnika (zielen malachitowa) i zanieczyszczenia organicznego (fenol) oraz ocena działania lub prawdziwości modelu przy zastosowaniu stałego złoża adsorpcyjnego. Do wstępnej selekcji adsorpcji adsorbatu użyto izoterm, aby zbadać skuteczność adsorpcji a także granicę maksymalnej ilości, która może być zaadsorbowana przez określoną jednostkę. Jednakże izotermie adsorpcji nie mogą oddać dokładnej skali danych uzyskanych na instalacji ze stałym złożem, ponieważ: (i) adsorpcja w kolumnie nie jest w stanie równowagi, (ii) adsorbet rzadko zostaje całkowicie wyczerpany w czasie prowadzenia procesów na skalę przemysłową, (iii) wpływ recyrkulacji pozostaje nie znany, (iv) izotermie nie mogą przewidywać zmian chemicznych lub biologicznych zachodzących na adsorbencie.

W związku z tym zbadano praktyczne zastosowanie adsorbatu 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 ziareń popiołu lotnego oraz wzrostem temperatury. Wykonano badania na systemie kolumnowym z zastosowaniem jednoskładnikowego roztworu zieleni malachitowej oraz próbek dwuskładnikowych i wyznaczono pojemność do punktu przełomania. 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 kolumna może być używana przez 20 cykli adsorpcja-regeneracja bez utraty pojemności adsorpcyjnej.