Dynamic adsorption of phenol using modified coal fly ash

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Abstract—Packed bed column adsorption is an efficient and cost effective process for removing various pollutants from industrial effluent. Coal fly ash (CFA) generated from coal-burning power plants may pose serious implications on the economy and environment. MCFA was synthesized from CFA, by hydrothermal alkali treatment method. MCFA was reported to be amorphous, with 43.72% Al₂O₃ and structure of aluminosilicate matrix. In the present study, MCFA is used as an adsorbent in packed bed column for sequestering phenol. The column was operated at varied phenol concentration (70.0, 292.7, 651.2, 1039.9 mg/l) with variable flow rate (0.375, 0.75, 1.0 ml/min), using different bed height (7.5, 13.5, 27.5 cm). Local pulp and paper mill effluent containing 78 ppm phenol was percolated through 13.5 cms bed height column (10g MCFA) at flow rate of 1ml/min rate, study showed that column was saturated after 8hrs feeding, which removed 2.378 mg/g of phenol (30% phenol) from paper effluent. In insitu dynamic column removal of phenol was reported to be lower than pure standard phenol feed under similar experimental condition, that may be attributed to commutitive adsorption of pollutants. Packed bed column of MCFA may be deemed as comparatively cheaper adsorbent for removal of phenol from phenol rich effluent like textile industry. Modified Coal Fly Ash (MCFA), may herald an interesting promise as comparatively cost-effective adsorbent for removal of phenol from phenol rich industrial effluent. The scale up design parameters of wider diameter column can be estimated as 13.5 cm bed height, 12.24 cm column diameter (d) with surface area of 117.75 cm², which can be packed with 3388.17 grams of MFCA adsorbent, which can be operated at 150 cm²/min flow rate.

Key words— MFCA,CFA, Phenol, packed bed column, adsorption, Thomas, Yoon-Nelson and Adams-Bohart model, textile effluent, pulp and paper effluent, break-through curve

1. INTRODUCTION

Effluents from the various chemical industries contain some organic and inorganic chemicals which creates environmental pollution. Phenolic waste water pose serious environmental problem and contaminated water require pre-treatment to safe level, before releasing into the water bodies or its use [1]. Phenolic compounds have been classified as high-priority pollutants as per Environmental Protection Agency (USA) [2]. Phenolic effluent is generated through plastic processing, pharmaceutical, petrochemical, paint, paper & pulp, and textile industries. Phenolic pollutants at low concentrations, are harmful to water bodies and humans, and are placed in list of priority pollutants [3, 4, 5].

In India, Coal fly ash (CFA) is generated through coal based thermal power station in electricity generation, to the extent of 200 million tons of fly ash per year, sharing 61.5 percent of total power generated [6]. In the year 2012, the power generation in India was about 200,000 MW, which is expected to increase up to 300,000 MW by 2017. CFA is exploited for various use in cement and concrete industry as an additive, treatment of acid mine drainage as well as in reclamation and restoration of land [7, 8]. Coal fly ash can be converted into zeolite, which is quite attractive approach mitigates fly ash pollution [9]. In present work a study, Modified Coal Fly Ash (MCFA)/artificial zeolite, was synthesized from CFA by hydrothermal alkali treatment to be used as adsorbent for removal of phenol.

Packed bed column of MCFA was used for adsorbing pollutants (phenol) by continuous flow of the influent from the top on the bed of adsorbents, and continuous withdrawal of the treated effluent from bottom. Packed bed column adsorption offers an ease in operation, high yields and high liquid residence time, and is preferred over batch adsorption and, can be scaled up from a laboratory setup [10].

Hence, an organized design for scale up of adsorption column investigation of the phenol adsorption on MCFA was reported in this study. Also the design optimum operating parameters of column were established in terms of packed bed length, feed flow rate and initial phenol concentration. The prediction of the breakthrough curves and the validation to different packed bed models like Thomas, Yoon-Nelson and Adams-Bohart models were studied to decipher nature of adsorption processes.

2. MATERIALS AND METHODS

2.1 Adsorbate

Fresh aqueous phenol solution (70.0, 292.7, 651.2, 1039.9 mg/l), was prepared by diluting the required quantities of phenol in the distilled water to obtain adsorbate solutions of various initial concentrations (Cₒ).

2.2 Adsorbent

MCFA was prepared by taking 100 grams of <75 micron size CFA and 50 grams of aluminium oxide (Al₂O₃), mixed with 1000 ml of 5N NaOH solution in a glass beaker (Fig. 4.3). This solution was kept for crystallization for 48 hours with continuous stirring at 80°C. Separated MCFA crystals were washed several times with distilled water till pH of washed water become neutral to ensure complete removal of NaOH traces. Neutralized crystals were further air dried to remove the excess moisture. Complete dried MCFA adsorbent was procured after drying in oven at 100°C for one hour. This dried MCFA adsorbent was stored in the air tight polyethylene bags for further experimentations [11].

2.3 Characterization of MCFA
Different sophisticated instruments like SEM, FTIR, XRD and XRF are used for characterization, surface morphology, mineralogical compositions, and elemental analysis of MCFA [11].

2.4 Experimental Investigations

MCFA was packed in the glass column having 45 cm length and 10 mm internal diameter with the support of glass bed and cotton wool at the bottom of the column. The column was operated under down flow condition which allows the influent to be gravity fed, which results in the maximum contact between the MCFA and the influent. The experiments were conducted for the effect of bed height (7.5, 13.5, 27.5 cm), flow rate (0.375, 0.750, 1.0 ml/min) and initial phenol concentration (70.0, 292.7, 651.2, 1039.9 mg/l) on the adsorption by assessing the breakthrough curve. The pH of the influent was kept at 6.0 for all the experiments. Effluent from the bottom of the column was collected with fixed interval of time for phenol concentration which was determined by UV spectrophotometer.

2.5 Packed Bed Column For Paper Effluent

MCFA was packed in the glass column having 45 cm length and 10 mm internal diameter with the support of glass bed and cotton wool at the bottom of the column. The column was operated under down flow condition which allows the industrial waste water which is collected from local pulp and paper mill effluent containing 78 mg/L phenol concentration to be gravity fed, which results in the maximum contact between the MCFA and the waste water. The experiments are conducted at 13.5 cm MCFA bed height and 1.0 ml/min flow rate for assessing the breakthrough curve. The pH of the influent was kept at 7.0 for the experiments. Effluent from the bottom of the column was collected with fixed interval of time for phenol concentration which was determined by UV spectrophotometer.

2.6 Estimation of Adsorption Parameters

The various process parameters such as breakthrough capacity (qB), saturation capacity (qS), volume of effluent treated (Vef), removal efficiency (RE), mass transfer zone (MTZ) and fractional bed utilization (FBU) were investigated to evaluate the column performance. The breakthrough curves are drawn by plotting residual phenol concentration versus time [12].

2.7 Performance of Packed Bed Column

2.7.1 Thomas Model

The Thomas model is frequently applied to calculate the adsorption capacity of adsorbent and predict break through curve assuming the second order reversible reaction kinetics and the Langmuir isotherm [13, 14]. Linear form of Thomas model is given as under

\[
\ln \left( \frac{C_0}{C_t} - 1 \right) = K_{TH} q_0 M / Q - K_{TH} C_0 t
\]

Where, \( C_0 \) is initial phenol concentration (mg/L), \( C_t \) is effluent phenol concentration at time \( t \) (mg/L), \( K_{TH} \) is Thomas model constant (L/min.mg), \( q_0 \) is prediction adsorption capacity (mg/g), \( M \) is mass of adsorbent (g) and \( Q \) is inlet flow rate (ml/min). The value of \( K_{TH} \) and \( q_0 \) are determined from slope and intercept of a plot of ln \( (C_0/C_t - 1) \) versus \( t \).

2.7.2. Yoon - Nelson Model

The main aim of Yoon-Nelson model is to predict the time of column run before regeneration of column becomes necessary. According to this model, the amount of phenol adsorbed in a packed bed is half of the total phenol entering the adsorbent bed within time period \( 2 \bar{T} \), where \( \bar{T} \) is the time required for 50 % break through. Linear form of Yoon-Nelson model is given below [15].

\[
\ln \left[ \frac{C_t}{(C_0 - C_t)} \right] = K_{YN} t - \bar{T} K_{YN}
\]

Where, \( C_0 \) is initial phenol concentration (mg/L), \( C_t \) is phenol concentration at time \( t \) (mg/L), \( t \) is flow time (min), \( \bar{T} \) is time required for 50 % breakthrough (min) and \( K_{YN} \) is Yoon-Nelson rate constant(L/min). The values of \( K_{YN} \) and \( \bar{T} \) are determined from the slope and intercept of ln \( [C_t/(C_0 - C_t)] \) versus \( t \).

2.7.3. Adams-Bohart Model

The model is used in describing the initial part of the breakthrough curve [10, 17]. The model explains that the kinetics was controlled by external mass transfer in the initial part of adsorption [18]. This model is also based on the postulate that the adsorption rate is proportional to the residual capacity of adsorbent and the solute concentration [19, 20, 21]. The expression for the model is given by

\[
\ln \left( \frac{C_t}{C_0} \right) = k_{AB} C_0 \delta - \frac{[(k_{AB} N_0 Z)/\delta]}{\gamma} - \frac{[(k_{AB} N_0 Z)/\delta]}{\gamma}
\]

Where, \( C_0 \) is the inlet concentration of phenol (mg/L), \( C_t \) is the outlet concentration of phenol (mg/L), \( k_{AB} \) is the kinetic constant (L/mg.min), \( \delta \) is the linear velocity (cm/min), \( Z \) is the length of the bed (cm) and \( N_0 \) is the saturation concentration (mg/L).

The values of \( k_{AB} \) and \( N_0 \) were determined from the slope and intercept of the linear plot of ln \( (C_t/C_0) \) against time \( t \).

2.7.4. Error Analysis

To find the best fit model for the packed bed column adsorption study, error analysis was also performed. The error functions used for are the following. The Chi square statistic test \( (\chi^2) \) [22]

\[
\chi^2 = \sum_{i=1}^{n} \left[ \frac{[(C_t/C_0)_{\text{cal}} - (C_t/C_0)_{\text{exp}}]^2}{(C_t/C_0)_{\text{exp}}} \right]
\]
and the least square of errors (SSE) [17]

\[ SSE = \sum_{i=1}^{n} [(C_i/C_0)_{\text{cal}} - (C_i/C_0)_{\text{exp}}]^2 \]  

Where \((C_i/C_0)_{\text{cal}}\) and \((C_i/C_0)_{\text{exp}}\) are the calculated and the experimental dimensionless concentration values.

2.8 Designing of Packed Bed Column for Scale-up

Packed bed column can be designed using two approaches; scale-up procedure and kinetic approach. In both approaches the breakthrough curve from test column, of laboratory scale is required and the column should be as large as possible to minimize side wall effects. In this study, scale up approach is used for design of the column.

3. RESULTS AND DISCUSSION

3.1 MCFA Characterization

SEM image of MCFA showed the structural break down of larger particles and increased surface roughness and pore volume [11]. FTIR analysis showed, the pore opening reported due to Si-O and Al-O internal tetrahedron vibrations with shifting of the Si/Al-O at lower frequencies band. Increased crystallinity ascertained by higher absorbance, with O–H peak obtained at 3246-3569 cm\(^{-1}\) [11]. The XRD showed, higher SiO\(_2\) concentration, revealed by large characteristic peaks of quartz (SiO\(_2\)). Increased volume of micropore may be attributed to breaking of Si-Al chain in CFA [11]. The XRF analysis of MCFA confirmed its composition as 44.63% SiO\(_2\), 43.72% Al\(_2\)O\(_3\) and 0.620 % Na\(_2\)O, which is synonymous to zeolites [11].

3.2. Effect of operating parameters

3.2.1. Effect of Bed Height

It was observed that the breakthrough time and bed exhaust time increases with increase in bed height. For the bed height of 7.5, 13.5 and 27.5 cm and 30% breakthrough time with feed phenol concentration of 1039.9 mg/L was found as 65, 235 and 645 minutes, while for 70% breakthrough, the exhaust time was found to be 220; 658 and 1435 minutes respectively. It can also be observed that larger the breakthrough time, is associated with higher the breakthrough capacity of the column. The mass transfer zone (MTZ) and fractional bed utilization (FBU) increases as the bed height increases. It can be inferred that at higher bed height, higher MTZ and FBU could be obtained. Hence it can be concluded that longer packed bed height column is favoured for better column performance [12].

3.2.2. Effect of Flow Rate

It was observed that with lower flow rate the adsorption efficiency was higher. It was reported that with increased flow rate there is decrease in volume treated and the breakthrough efficiency. The faster breakthrough occurred at higher flow rates and thus the shortened bed service time was required for saturation of the bed. The relative breakthrough time and effective volume at any breakthrough point decreases as the flow rate increases. The optimum uptake capacity for flow rate of 0.375, 0.750 and 1.000 ml/min was found to be 31.512, 27.456 and 17.472 mg/g respectively at 80% saturation of the column. The mass transfer zone (MTZ) and fractional bed utilization (FBU) decreases as the flow rate increases. From this it can be inferred that at lower flow rate high MTZ and FBU could be obtained. It can be concluded that for better column performance is associated with lower flow rate [12].

3.2.3. Effect of Phenol Concentration

It was observed that as concentration increases from 70.0 to 1039.9 mg/L, the breakthrough time decreases from 515 to 274 minutes for 20% breakthrough. It suggest that higher phenol inlet concentration saturates the MCFA particles more rapidly. As the initial phenol concentration increases breakthrough time and effective volume treated decreases but breakthrough adsorption capacity increases. The mass transfer zone (MTZ) increases as the initial phenol concentration increases while fractional bed utilization (FBU) decreases. From this it can be inferred that at higher phenol concentration, high MTZ can be obtained but reduction in FBU was observed. It can be concluded that for better column performance lower concentration is favoured to get the maximum utilisation of the packed bed [12].

3.3. Modeling and Error Analysis

The three different models Thomas, Yoon-Nelson and Adms-Bohart models are studied for the better suitability of the models and from performance [12] and error analysis (Table 1), Thomas model was found to be the best suited for experimental conditions.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Thomas model</th>
<th>Yoon-Nelson Model</th>
<th>Adms-Bohart model</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Z) (cm)</td>
<td>(C_0) (mg/L)</td>
<td>(F) (ml/min)</td>
<td>(\chi^2)</td>
</tr>
<tr>
<td>7.5</td>
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<td>13.5</td>
<td>292.70</td>
<td>1.000</td>
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</table>
### 3.4 Packed Bed Column Study on Paper Mill Effluent

Local pulp and paper mill effluent containing 78 ppm phenol was run through 13.5 cm bed height column (10 g MCFA) at flow rate of 1 ml/min rate, study showed that column was saturated after 8 hrs., which removed 2.378 mg/g of phenol resulting (30% phenol of total pollutants). In situ paper mill effluent, phenol removal was shown to be lower than experimental phenol feed run under similar experimental condition that may be attributed to adsorption of other pollutants along with phenol [23].

### 3.5 Design of Dynamic Column for Scale up

Estimation of scale-up column design parameters:

**Laboratory Scale Data**

- Flow rate (Q) = 1 ml/min (1 cm³/min)
- Column diameter = 10 mm (1 cm)
- Column depth (packed bed) = 135 mm (13.5 cm)
- Density of MCFA = 2.1 g/ml (2.1 g/cm³)
- Breakthrough volume \( (V_{\text{breakthrough}}) \) = 114 ml (114 cm³) - 20% breakthrough
- Exhaustion volume \( (V_{\text{exhaustion}}) \) = 210 ml (210 cm³) - 80% breakthrough

#### a) Filtration Rate of the Laboratory Scale Test

\[
\text{Filtration rate (FR)} = \frac{Q}{A} \quad \text{(cross-sectional area)}
\]

\[
A = \pi \frac{d^2}{4}
\]

This same FR is applied to packed column.

#### b) Area of the Packed Column

\[
A = \frac{Q}{\text{FR}}
\]

If the set value of flow rate of the required packed column is 150 cm³/min., then:

\[
A = \frac{150}{1.27388} = 117.75 \text{ cm}^2
\]

Since, \( A = \pi \frac{d^2}{4} \), the column diameter can be calculated as

\[
d = \sqrt{\frac{4A}{\pi}} = \sqrt{\frac{4 \times 117.75}{\pi}} = 12.2435 \text{ cm}
\]

#### c) Empty Bed Contact Time (EBCT) of the Laboratory Scale Packed Column

\[
\tau (\text{EBCT}) = \frac{\text{Volume of bed}}{Q} \quad \text{(flow rate)}
\]

\[
\text{Volume of bed} = A \times \text{Height}
\]

\[
\tau (\text{EBCT}) = \frac{117.75 \times 13.5}{150} = 10.5975 \text{ min.}
\]

10.5975 minutes is the EBCT of the Packed Column.

#### d) Height of the Packed Column

\[
(\text{EBCT}) \tau \times \text{Filtration rate (FR)} = 10.5975 \times 1.27388 = 13.49994 \text{ cm} \approx 13.5 \text{ cm}
\]

This is the same as the height of the laboratory scale test column because height of a column is set by the empty bed contact time (\( \tau \)) and filtration rate and these are the same for laboratory scale test column and the packed column.

#### e) Mass of MCFA required in the scale-up Packed Column

\[
\text{Volume of the packed column} = \text{cross sectional area} \times \text{Height}
\]

\[
\text{Volume of the packed column} = (\pi \frac{d^2}{4}) \times \text{Height}
\]

\[
\text{Volume of the packed column} = (3.142 \times 12.2435^2)/4] \times 13.49994
\]

\[
\text{Volume of the packed column} = (3.142 \times 149.9045)/4] \times 13.49994
\]

\[
\text{Volume of the packed column} = (470.9961)/4 \times 13.49994
\]

\[
\text{Volume of the packed column} = 11738.26 \text{ ml} (1589.6049 \text{ cm}^3)
\]

Packed bed MCFA density is

\[
2.1 \text{ g/ml}
\]

Mass of the MCFA

\[
2.1 \times 1589.6049 = 3338.1703 \text{ g (3.3381703 kg)}
\]

#### f) Determination of \( q_e \) (Phenol Removed)

Mass of MCFA in the laboratory scale test column

\[
\text{Volume of column bed} \times \text{Density of MCFA}
\]

\[
10.5974 \text{ ml} \times 2.1 \text{ g/ml} = 22.2547 \text{ g}
\]

\[
0.0222547 \text{ kg}
\]
Total capacity (t) = Volume at exhaustion * Time to reach exhaustion
= 210 * 210
= 44100 ml (44100 cm$^3$)

Phenol removed by 22.2547 g of the MCFA = Total capacity/Mass of the adsorbent in the laboratory scale test
= 44100 ml/22.2547(g)
= 1981 ml/g
= (1981*1.07) g/g
= 2119.67 g/g
= 21.1967 mg/g

Phenol removal on actual laboratory scale test column is found to be 17.472 mg/g.

g) Fraction of Capacity Left Unused (Laboratory scale packed column)

Total capacity = 210 * 210 = 44100 ml
Phenol removed before breakthrough = 114 * 210 = 23940 ml
Fraction of capacity left unused (f) = (44100-23940)/44100
= 0.4571 = 45.71%.

This fraction of capacity left unused will apply to the packed column also.

h) Breakthrough Time of the Packed Column

Phenol loading rate = 210 * 150 = 31500 g/min
MCF A consumption rate = 31500/1981 = 15.90 g/min
Amount of MCF A consumed = 3338.1703 (1-0.4571)
= 1812.29 g.

Breakthrough time = Amount consumed/MCF A consumption rate
= 1812.29/15.90
= 113.98 min

This is the same as the packed bed column: 114 min.

i) Volume Treated Before Breakthrough

Volume treated = Flow rate * breakthrough time
= 150 * 113.98
= 17097 cm$^3$
= 17097 ml
= 17.097 Litre

4. CONCLUSION

It was observed that the column parameters like bed height, flow rate and phenol concentration significantly affects the column performance. Continuous removal of phenol by Packed Bed Column follows the Thomas model. Modified Coal Fly Ash (MCFA) column when operated at bed height of 13.5 cm, feed flow rate of 1ml/min at 70 ppm phenol concentration resulted in 80% break through time of 990 minutes. However MCFA column when operated at similar experimental condition resulted in 30% stand out phenol removal from paper effluent (78% phenol) at comparative shorter, 80% break through time of 305 minutes. Study suggests that if the large column diameter are designed and predicted, higher phenol removal in smaller breakthrough time can be expected under similar experimental conditions. The design parameters for packed column was found to be area as 117.75 cm$^2$, diameter(d) as 12.2435 cm and the mass of MCFA required as 3338.1703 grams for the flow rate of 150 cm$^3$/min.

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