Performance evaluation of coconut shell originated activated carbon as an adsorbent on the paint factory effluent treatment

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Abstract. The current study was aimed to evaluate the ability of the activated carbon prepared from coconut shell in the decolorization of paint factory effluent (PFE). The studies were performed in the fixed bed adsorption column by optimizing the design variables viz., initial effluent concentration, bed height and low rate. The experimental observations were used to make breakthrough curves and were validated using Adams–Bohart model and Yoon-Nelson model. The results recommended that the encapsulated activated carbon of coconut shell origin showcased its capacity to perform in the process of paint factory effluents decolorization as an adsorbent.

Keywords: coconut shell; activated carbon; paint factory effluent; adsorption; fixed-bed adsorption column

1. Introduction

By blending solvent, pigment, binder and additives paint has been prepared. Though various types of paints are available in the market based on its application, the helpful way of analysing it in treatment point of view is based on the presence of primary solvent. The solvent could be either water or organic chemical, and sometimes absence of this is also possible. Generally there will not be much production waste from the paint unit, instead majority of the effluent sourced from the degreasing operation of numerous unit operations [1]. The disposal of such effluents without any treatment would certainly give hazardous effect to the water bodies, humans and to the environment, because of the existence of the toxic pollutants, heavy metals and so on. To consider the environment and the law, the developed wastewater is to be treated before disposal [2].

Various traditional techniques are available for the removal of a pollutant from PFE. It was effectively treated using the plant-based materials S. potatorum and C. opuntia as a natural coagulant [3, 4]. When weighing the traditional techniques against each other, it was found that the adsorption process was more economical, efficient and simple. Researchers have also studied the potentiality of the agro-based adsorbent S.potatorum, encapsulated form of C. opuntia and a seafood processing waste P. sanguinolentus (crab shell) as an adsorbent in the treatment of paint industry wastewater. [5-7]. Activated carbon adsorption has been the most popular and effective method for removing color and heavy metals from water and wastewater.
The large surface area, high porosity, a considerable amount of mechanical strength and a high degree of surface reactivity make activated carbon an ideal adsorbent. However, the cost factor imposes restrictions on its application in the paint industry [8]. Researchers today focus mainly on achieving maximum removal of pollutant ions by using low-cost and plentifully available materials. The treatment efficiency lean on selection of an adsorbent and its universal availability. In this aspect either a natural material or an industrial waste could be the better choice [9].

The modified coconut shell activated carbon via pyrolysis and by magnetic operation were successfully used for the removal 2-nitrophenol (2-NP). The observed adsorption capacity was 103 mg/g [10]. The nanoporous coconut shell activated carbon were experimented on the removal of methylene blue (MB) in the batch operations [11]. In the treatment of Bi (III), the coconut shell activated carbon expelled its adsorption efficiency as 98.72% [12]. Being a cheaper source as well as an effective adsorbent, it has also been used in the removal of sodium dodecyl benzene sulfonate [13], toluene and chlorobenzene [14] and heavy metals [15].

In the present study, an attempt has been made to use the, activated carbon prepared using coconut shell as an adsorbent in the treatment of PFE using a fixed-bed adsorption column. The operational variables were selected as the initial concentration of the effluent, bed height, and inlet flow rate. The performance was evaluated through decolorization.

2. Materials and methods

Materials

Adsorbate

The paint factory effluent (PFE) was re-created in the laboratory by blending the white primer and the blue shaded paint in different ratios. Three samples are prepared with an initial concentration (mg/L) of 1200, 1350 and 1850 and specified as Sample number 1-3, respectively. The Physio-chemical properties of the PFE are given in Table 1.

| Sample number | Initial COD (mg/L) |
|---------------|-------------------|
| 1             | 1200              |
| 2             | 1350              |
| 3             | 1850              |

Adsorbent

The activated carbon produced from Coconut shell with a size of 0.5 mm was procured from Sakthi chemicals, Erode (Fig.1).
To perform the lab scale continuous adsorption experiments, a fixed-bed column (FBC) was fabricated using Pyrex glass of dimension 2 cm diameter and 50 cm length (Fig.2). The feed was opened in the down flow mode at room temperature with the aid of peristaltic pump (Ravel Hitek, India).

Methods

Formation of immobilized beads
The uniform sized coconut shell powder was encapsulated using sodium alginate. 3 % (w/v) of activated carbon powder and 1 % (w/v) of sodium alginate was blended using a distilled water and were driven out as a drop using a medical syringe into the 3% CaCl₂ solution. For the sake of hardening the beads this was kept in the refrigerator for 24 h at 4°C. The excess Calcium ions were removed by washing the beads with de-ionized water. For the control studies, the encapsulated beads were formed using the sodium alginate in the absence of activated carbon [8].

Experimental setup
The bottom of a fixed-bed column (FBC) was tapered and given with control valve for the collection of treated sample. The arrangements were made in the following manner from the bottom of a FBC. (i) Glass wool (to deflect the blockage of beads into the tapered end) (ii) glass beads for 1 cm height ( as a hold for the encapsulated beads) (iii) The encapsulated activated carbon to the desired height and (iv) glass beads for 1 cm height (to maintain even adsorbate flow)

Throughout the experiments the temperature and the initial pH was not altered. To bring the consistency in the packing for each trial, it was practiced to fill the distilled water till the half length of a FBC and a weighed mass of beads were admitted smoothly. After attaining the required bed height the water was drained out. According to the theory of terminal settling velocity, almost near to uniform, close and regular packing were maintained for every run. The sample was collected at proper gap to measure the residual colour.

At the time of saturation the run was stopped and the column was replaced with the fresh beads. Each study was performed thrice to check the reproducibility. The values reported in the figures were the mean of three data points. The experiments were reiterated to examine the impact of the initial concentration of PFE, bed height and flow rate on decolorization efficiency [9].

Performance analysis
The treatment efficiency was assessed to remove color, using SL 218 double UV visible spectrophotometer (Elico – India) at λmax 612 nm.
3. Results and discussions

*Effect of operational parameters on breakthrough curves*

The equations used to analyse the process parameters of an FBC are given in Table 2. The influence of operating variables on an FBC design parameter is summarized in Table 3.

**Table 2** Process analysis parameters of a FBC

| Volume of effluent treated, mL | $V_{eff} = Qt_t$ |
|--------------------------------|------------------|
| Empty bed residence time (EBRT), min | $\frac{Bedvolume}{Volumetric flowrate of the effluent}$ |
| Total quantity of solute adsorbed for a given $C_o$, $Q$, mg | $q_t = QC_o \int_0^{t_z} \left(1 - \frac{C_t}{C_o}\right) dt$ |
| Total colour removal % | $\frac{q_t 1000}{C_o Q t_t}$ |
| mass transfer zone or equivalent length of unused bed (MTZ), cm | $H \left(1 - \frac{t_b}{t_s}\right)$ |

**Table 3** Influence of operating variables on a FBC design parameters

| Co (mg/L) | Q (cc/min) | H (cm) | $t_t$ (min) | qt (mg/g) | $t_b$ (min) | ts (min) | $V_{eff}$ (mL) | EBRT (min) | Total color removal % | MTZ (cm) |
|-----------|------------|--------|--------------|-----------|-------------|----------|----------------|------------|---------------------|----------|
| 1200      | 5          | 15     | 600          | 2.22      | 125         | 550      | 3000           | 9.420      | 61.60               | 11.6     |
| 1350      | 5          | 15     | 575          | 3.03      | 75          | 500      | 2875           | 9.420      | 78.07               | 12.8     |
| 1850      | 5          | 15     | 400          | 3.79      | 25          | 400      | 2000           | 9.420      | 82.00               | 14.1     |
| 1200      | 5          | 10     | 450          | 1.36      | 25          | 325      | 2250           | 6.280      | 50.19               | 9.2      |
| 1200      | 5          | 25     | 775          | 2.74      | 225         | 675      | 3875           | 15.70      | 78.82               | 16.7     |
| 1200      | 10         | 25     | 600          | 6.16      | 125         | 550      | 6000           | 7.850      | 85.52               | 19.3     |
| 1200      | 15         | 25     | 375          | 9.44      | 50          | 350      | 5625           | 5.233      | 58.00               | 21.4     |

*Effect of initial concentration*

The three expanding levels of introductory PFE concentration were 1200, 1350 and 1850 mg/L. The accompanying four parameters were decreased with the ascent in effluent concentration: (i) breakthrough time (from 125 to 25 min); (ii) total adsorption time (from 600 to 400 min); (iii) total volume of effluent handled (3000, 2875 and 2000 mL). The colour removal efficiency was raised from 61.60% to 82%. Void bed residence time stayed undisturbed by alters in initial concentration and kept up as 9.420 min. The maximum pollutant uptake was raised (2.22, 3.03, 3.79 mg/g) (Table 3, Fig. 3).
It was marked that higher pollutant concentration narrowed the breakthrough time and volume by marginally restraining mass-transfer flux from the mass adsorbate to the encapsulated bead surface, likely brought about by more fragile driving thrusts. Breakthrough curves got more extreme subsequently. Elevating the concentration boosted the accessibility of contamination particles for adsorption by dynamic locales, guaranteeing higher take-up regardless of breakthrough time being more limited than at smaller concentrations [16]. An expansion in the initial concentration prompted early saturation, achieving the breakthrough time's speedier appearance. The explanation was a decrease in mass transportation, spoken to by a declivity in diffusion coefficient and mass exchange coefficient at low concentrations. It was seen that at a higher initial concentration of adsorbate, adsorption destinations became soaked quickly, prompting a more limited breakthrough time. Alternately, an advancement was deferred for a lower pollutant concentration and the adsorbent surface set aside a long effort to get exhausted [17].

Fig. 3. Effect of initial concentration of effluent on color removal in a FBC
Bed height: 15 cm; Flow rate: 5 cc/min; Initial conc.: 1200 -1850 mg/L

Effect of bed height
Bed height acts as a basic property while planning an adsorption section to treat explicit loads of pollutants in effluent and lacking bed height would bring about helpless adsorption behavior it identifies with the quantity of dynamic sites accessible for adsorption. To show the impact of bed height with the assistance of an experimental breakthrough curve (Fig. 4), this parameter fluctuated somewhere in the range of 10 and 25 cm, while keeping up stream rate (5 cc/min) and initial concentration (1200 mg/L) of effluent as consistent, without modifying the initial pH. The absolute time, comparing to the column's stoichiometric limit, was discovered to be improved with an ascent in the bed range from 450 to 775 min (Table 3). The shape of the breakthrough curve relies upon the bed height and mass of the adsorbent. The steady expansion in the volume of the fluid arrangement with an increment in bed height was because of more sorption locales. This implies that the more noteworthy the bed height, the more the mass of adsorbent and the better it's ability for adsorbing colorants from PFE [18].
Fig. 4. Effect of bed height on color removal in a FBC

Bed height: 10-25 cm; Flow rate: 5 cc/min; Initial conc.: 1200 mg/L

Effect of inlet flow rate

The absolute time consumed to direct each run demonstrated a descending pattern as the stream rate ventured up as 5, 10 and 15 cc/min. The complete adsorption total time and breakthrough time were 775, 600 and 375 min and 225, 125 and 50 min for stream rate estimations of 5, 10 and 15 cc/min, independently. More extreme and quicker advancement bends arose with a quicker stream rate. The overall colour removal relating to the column's stoichiometric limit was found to decrease from 78.82% to 58%, with a height in the stream rate (Fig.5) [19]. The all out volume of the treated water expanded from 3875 to 5625 mL. The take-up of contamination was most extreme in the underlying stages and turned out to be steadily lower, lastly, the adsorbent arrived at the saturation point. Bringing down the stream rate delayed contact time but limited the adsorption zone. At the point when the volumetric stream rate modified as an ascending order, the breakthrough curves became more extreme and arrived at the breakthrough point in a more limited period. This might be on the grounds that (a) the expansion in contamination load brought about quick saturation and (b) the decline in the residence time between the adsorbent and adsorbate in the column forestalls the dispersion of adsorbate on the adsorbent pores. The connection time among contamination and adsorbent was exceptionally concise at higher stream rates, bringing about a fall in removal efficiency (Table 3). To summarize, it very well may be said with assurance that the adsorbent got saturated rapidly at a higher linear stream rate due to the higher contamination load and more limited contact time. The outcomes have concurred with eliminating Cu²⁺ from the arrangement utilizing agricultural residue rice husk in the adsorption studies [20].
Fig. 5. Effect of inlet flow rate on color removal in a FBC
Bed height: 25 cm; Flow rate: 5–15 cc/min; Initial conc.: 1200 mg/L.

Modelling of breakthrough curves
The linearized models for the breakthrough curves were given in Table 4. In Table 5, parameters of breakthrough models in a FBC at various conditions were tabulated.

Table 4 Breakthrough curve models for a FBC

| Model               | Equation                                                                 |
|---------------------|---------------------------------------------------------------------------|
| Adams-Bohart        | \( \ln \left( \frac{C_t}{C_o} \right) = (k_{AB} C_o) t - \frac{k_{AB} N_o H}{U_o} \) |
| Yoon-Nelson model   | \( \ln \left( \frac{C_t}{(C_o - C_i)} \right) = k_{YN} t - k_{YN} \tau \)    |

Table 5 Influence of operating variables on breakthrough model parameters

| Co (mg/L) | Q (cc/min) | H (cm) | k_{AB} (L/(min.m g)) | No | R² | k_{YN} | τ (min) | R² |
|-----------|------------|--------|----------------------|----|----|--------|--------|----|
| 1200      | 5          | 15     | 0.0045               | 69 | 0.8945 | 0.0085 | 413     | 0.9714 |
| 1350      | 5          | 15     | 0.0022               | 108 | 0.9056 | 0.0058 | 527     | 0.9428 |
| 1850      | 5          | 15     | 0.0011               | 130 | 0.8998 | 0.0042 | 566     | 0.9737 |
| 1200      | 5          | 10     | 0.0008               | 132 | 0.5692 | 0.0031 | 178     | 0.6696 |
| 1200      | 5          | 25     | 0.0031               | 55 | 0.7675 | 0.0071 | 513     | 0.9207 |
| 1200      | 10         | 25     | 0.0017               | 108 | 0.8464 | 0.0047 | 408     | 0.9157 |
| 1200      | 15         | 25     | 0.0009               | 155 | 0.5123 | 0.0029 | 154     | 0.5765 |
Adams–Bohart model

This Adams-Bohart mathematical expression for adsorption was operated on the data observed from the every experimental run to portray the initial part of the breakthrough curve. The kinetic constant $k_{AB}$ and adsorbent’s adsorption capacity $N_0$ was resolved from the linearized plot's intercept and slope (Fig. 6-8). Table 5, the estimations of $k_{AB}$ diminished with an expansion on the pair $C_0$ and $Q$, however it expanded along increment in bed heights. This indicated such general process kinetics was led by outer mass transfer in the entry of FBC [18]. In light of more overloaded destinations, the adsorption limit of the adsorbent $N_0$ expanded with expanding flow rate. Likewise, the kinetic constant $k_{AB}$ diminished with expanding flow rate [5]. This model gives a complete and basic way to deal with running and assessing the adsorption execution. Nonetheless, its legitimacy is restricted by the scope of conditions utilized.

Fig. 6. Influence of initial concentration of effluent on color removal - Adams- Bohart model

Fig. 7. Influence of bed height on color removal - Adams- Bohart model
This mathematical model depends upon the hypothesis that the diminishing rate in the probability of adsorption of adsorbate and its breakthrough on the adsorbent. The model rate constant $k_{YN}$ and the time needed for half adsorbate removal $\tau$ were determined (Fig 9-11). $k_{YN}$ was gained at a higher flow rate, initial concentration and minimal bed height. Additionally, $\tau$, diminished with an expansion in flow rate, $C_0$, and $H$ (Table 5). This is on the grounds that the expansion in initial concentration expands the opposition between adsorbate atoms for the adsorption site, eventually expanding the take-up proportion [6].
4. Conclusions

From the current examination results, it was seen that the activated carbon got from the Coconut shell was demonstrated its reasonableness to go about as an effective adsorbent in the decolorization of the paint factory effluent. The optimized boundaries from the continuous adsorption studies were summed up as,

i. The declourization was noticed to ascend with an expansion in the mass of the adsorbent, which is represented as bed height (10-25 cm) and drop with an expansion in effluent stream rate (5-15 mL/min) and effluent initial concentration (1200-1850 mg/L).

ii. The presence of an enormous number of actives sites (because of more impressive bed tallness), higher mass exchange slope (because of greater initial concentration) and more abundant contact time (because of reduced stream rate) brought about a higher adsorption limit.

Breakthrough bends were adapted with the bends of the Adams-Bohart model and Yoon-Nelson model.

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List of symbols and abbreviations

| Symbol | Description |
|--------|-------------|
| $C_{0}, C_t$ | Concentration of the solute, at $t=0$ and time ‘$t$’ in the effluent (mg/L) |
| $d$ | Mean diameter of immobilized beads (cm) |
| $H$ | Bed height (cm) |
| $k_{AB}$ | Kinetic constant in the model Adams-Bohart (L/(min . mg)) |
| $k_{YN}$ | Kinetic constant in the model Yoon-Nelson (1/min) |
| $N_o$ | Maximum adsorption capacity per unit volume of adsorption column(mg/L) |
| $Q$ | Inlet feed flow rate (mL/min) |
| $q_t, q_e$ | Total quantity of pollutant adsorbed at time ‘$t$’ and at equilibrium (mg/g) |
| $R^2$ | Correlation coefficient |
| $R_L$ | Separation factor |
| $t, t_b, t_s, t_t$ | Time, breakthrough time, saturation time, total time taken in FBC(min) |
| $U_o$ | Linear velocity of inlet effluent (cm/min) |
| $V, V_{eff}$ | Volume of effluent, Volume of effluent treated (mL) |
| $\tau$ | Time required for 50% adsorbate breakthrough time in Yoon-Nelson model (min) |