Utilization of Agronomic Wastes as Biosorbent for Removal of Dyes from Effluent

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TITLE OF THE THESIS:

Utilization of agronomic wastes as biosorbent for removal of dyes from effluent

ABSTRACT:

Management of water from industrial wastewater is a major concern for the environment. In this country, with enormous increase in demand of various chemical products leading to release huge quantity of hazardous pollutants to the aquatic environment. A liquid effluent containing dye can be considered as one of the prime sources of water pollution, likely to be generated from textile, paper, leather and paint industries. The management of wastewater effluent containing dye can be best addressed using adsorption technique. Due to high surface area and good porosity, activated carbon (AC) can be considered as one of the best adsorbent material for this kind of treatment. However, cost of conventional commercial AC generated from wood, bone, coconut shell etc. being high, renewable precursors such as agro-waste and industrial waste are aspiring alternatives. The technology minimizes the waste disposal problem and also serves as cost effective industrial wastewater treatment method.

In the current thesis, three abundantly available agro-wastes, millet cob husk, empty cotton boll, mustard husk were selected for preparation of AC by single step chemical activation method. Potassium hydroxide (KOH) was used as the chemical activating agent. The preparation parameters i.e. activation temperature, impregnation ratio and holding time were optimized by Response Surface Methodology (RSM). The prepared ACs from all three agro-wastes at optimum condition were characterized by various analytic techniques like proximate and ultimate analyses, Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and Brunauer-Emmett-Teller (BET) analysis.

Batch adsorption study for the removal of Methylene Blue (MB) and Reactive Orange 84 (RO84) dyes by the ACs were carried out. The effect of different process parameters such as initial dye concentration, pH, contact time, adsorbent dosage and temperature on the removal of dye was studied. The adsorption isotherm, kinetic and thermodynamic study was also done in the study, along with fixed bed column adsorption study. In this, the effect of initial flow rate, initial concentration of dye and bed height of the column was determined along with application of four different kinetic models. The dye adsorption processes were modeled using Designing of
Experiments (DoE) by using central composite design (CCD). The distinct advantage of factorial design was to reduce the number of experiments in order to obtain the best overall optimization process. Five-level and five factors CCD were applied to develop the model equations for MB and RO84 removal by using Design expert software (version 10.0.6).

**Graphical Abstract:**
State of the Art of the Research Topic:

Today, the major source of water pollution is the effluent generated by various process industries. Dye and textile processing industry require huge quantity of water and hence generate wastewater in large quantities [1]. More than 10,000 different types of dyes are produced commercially and the annual production of dye stuff is more than 7 lac tonnes per year [2]. Dye is an important ingredient for industries like textiles, paper, rubber, plastics, leather, food, pharmaceuticals etc. to colour their products [3-6]. Approximately 150 Mm$^3$ of effluent is produced by textile processing industry annually which contains 10 to 15% dyes [7]. Some of these dyes are toxic to human life [8]. Also, photosynthesis activity of aquatic life and micro-organism is adversely affected because of absorbing and reflecting sunlight by dyes in water [9].

Different technologies like adsorption, coagulation, Fenton’s process, advance oxidative processes, membrane filtration, electro-chemical process, etc. are presently used for the treatment of dye-loaded wastewater [10,11]. Out of these, one of the most effective technologies is adsorption because of its ease of operation and economic viability from industry viewpoint. AC is a popular adsorbent; however commercial AC is generally prepared from the conventional sources like lignite, peat and coke, etc. which are non-renewable sources.

The present study focuses on preparation of cost effective carbon adsorbents which are alternative to commercial ACs. There are many reported work by researchers using different kind of agro-wastes. However several agro-wastes are also used as animal fodder and also for preparing bio fertilizer. Millet cob husk, empty cotton boll and mustard husk were selected as precursor in the current research work to avoid the “food” issue. India is one of leading countries for production of millet, cotton and mustard. To the best of our knowledge, study on AC from the above mentioned precursors has not yet been reported.

In the single step chemical activation method using KOH to prepare AC from the precursor, the activation temperature, impregnation ratio and holding time are the main affecting parameters of the process. These parameters also affect the quality and quantity of the product. Looking into the literature, reports on optimization of process parameters for the production of AC using agro-wastes is limited. The modeling of preparation from agro-wastes was carried out by using Design of Experiments (DoE). A five-level and three-factor CCD was employed for the process modeling. Different process parameters mentioned above were taken as variables for the designing the experimental matrix. Effects of main factors and their interactions on the response
were estimated. Optimization was carried out using Desirability (D) function to estimate the optimum conditions to achieve better response i.e. % yield and performance in terms of dye uptake.

On the other hand, adsorption parameters such as dye solution pH, adsorption temperature, dye concentration, adsorbent dosage and adsorption time, greatly control adsorption of dyes on ACs. For the development of dye removal process in an industrial-scale, these variables need to be optimized. Due to several advantages associated with RSM over conventional one-factor-at-a-time (OFAT) method, it was selected to scrutinize the interactive effect of process variables on desired responses. Many researchers have made attempt to elucidate the effect of some of these parameters on dye adsorption on ACs derived from various agro-residues by OFAT method [12-18]. However, reported RSM approach is scant [19-20].

**Definition of the problem:**

The present research work addresses the following problems.

1. Conversion of non-fodder agro-residues into AC through a single step method using optimization technique.
2. To study the theoretical aspects like kinetics by column studies and thermodynamics of the adsorption process.

**Objective and scope of research:**

The main objective of this research is the preparation of ACs from selected agro-wastes i.e. millet cob husk, empty cotton boll and mustard husk for the effective removal of simple (MB) and complex (RO84) dyes from solution.

The specific objectives of this work are:

- To prepare AC from selected agro-wastes using single step chemical activation method.
- To optimize and analyze the effect of process parameters on the preparation of AC using RSM.
- To formulate mathematical model of AC preparation from agro-wastes by design of experiment software by using CCD.
- To compare all physico-chemical characteristics of the prepared ACs with their precursors.
- To build kinetic and isotherm adsorption models based on the results.
To remove dyes from aqueous phase by ACs developed at optimum conditions and to evaluate the effect of different process parameters such as pH, initial concentration of dye, dosage of adsorbent, temperature and time using RSM.

To regenerate spent AC using simple and economically feasible techniques.

To carry out techno-economic study.

Scope of the study:

The present research work has the possibility to serve as a solution to dye pollution in aqueous phase. Also, it can generate an efficient process for the utilization of agro-wastes into useful product such as AC which is an industrial chemical.

Original contribution by the thesis:

The original contribution is manifested by international peer-reviewed paper. Two papers have been accepted for publication as mentioned below. Another one paper of this work has been submitted and it is under review.


2. Samir Charola, Prasanta Das, Subarna Maiti. Dye adsorption using low cost carbon adsorbent from agrowaste-pearl millet cob husk Indian Journal of Chemical Technology (Accepted).


Achievements with respect to objectives:

Each objective of this research work was achieved. ACs with good porosity and high surface area were prepared from the selected agro-wastes. The process parameters for the preparation were optimized. At optimum conditions, there was a good agreement between predicted value and experimental value of responses. MB and RO84 dye was successfully adsorbed on prepared
ACs. The goal of regeneration of spent AC was also achieved. Mathematical model was developed for the maximum removal of dyes at optimized process parameters condition.

**Research methodology and Results:**
The methodology involved the experimental and modeling work.
The agro-wastes were collected from the field in western part of India. After cleaning and sun drying, they were characterized properly in order to check the suitability as precursor for the preparation of AC.

The modeling of preparation of AC from agro-wastes was carried out using RSM. Design of Experiments (DoE) software (version 10.0.6) was used for RSM study. A five-level and three-factor CCD was employed for process modeling. Three process parameters such as activation temperature, impregnation ratio and holding time were taken as variables for the designing of experimental matrix. Effects of main factors and their interactions on the response were estimated. Optimization was carried out using Desirability function to estimate the optimum conditions to achieve better response i.e. MB uptake and % yield.

The AC preparation variables and their operational range within which optimization was executed using RSM are shown in Table 1.

**Table 1:** Actual and coded values of preparation variables used for optimization

<table>
<thead>
<tr>
<th>Preparation variables</th>
<th>Unit</th>
<th>Code Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>-α</td>
</tr>
<tr>
<td>Activation Temperature</td>
<td>ºC</td>
<td>531.82</td>
</tr>
<tr>
<td>Impregnation ratio</td>
<td>-</td>
<td>1.32</td>
</tr>
<tr>
<td>Activation time</td>
<td>min</td>
<td>19.01</td>
</tr>
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</table>

The optimized AC from all three agro-wastes was characterized for proximate and ultimate analysis, BET analysis, SEM analysis, FTIR analysis. Then they were used for batch adsorption study for the removal of simple (MB) and complex (RO84) dyes. Adsorption variables pH, initial dye concentration, adsorbent dosage, temperature and time were studied.
Table 2: Actual and coded values of adsorption variables used for optimization

<table>
<thead>
<tr>
<th>Adsorption variables</th>
<th>Unit</th>
<th>Coded Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>-α</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>2.80</td>
</tr>
<tr>
<td>Initial dye concentration</td>
<td>mg/g</td>
<td>260</td>
</tr>
<tr>
<td>Adsorbent dosage</td>
<td>g/L</td>
<td>0.72</td>
</tr>
<tr>
<td>Temperature</td>
<td>K</td>
<td>300</td>
</tr>
<tr>
<td>Time</td>
<td>min</td>
<td>16</td>
</tr>
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</table>

Adsorption isotherm and kinetic study were also carried out. A study on fixed bed adsorption of RO84 dye by the AC prepared from empty cotton bolls was performed.

Results and Discussion:

Characterization of agro-wastes:

- The yield of AC mainly depends on fixed carbon. As per the proximate analysis, the fixed carbon % for empty cotton boll and mustard husk were 17.10 %, and 16.73 %, respectively making them suitable for preparation of AC. However, the value of fixed carbon % was 9.89 for millet cob husk. Nevertheless it is freely and abundantly available in India, therefore it was also taken as precursor of AC in this study.

- The ash % was below 9 % for all three agro-wastes which is a desirable characteristic. Ash consisting of inorganic salts which are converted to oxides at temperature of carbonization, could lead to blocking of the pores of AC. Hence, very high ash containing agro-wastes are not suitable.

- From ultimate analysis, the carbon % was in the range of 40-45 % which is desirable for AC preparation. The nitrogen % and sulfur % were well below 1 % for all three agro-wastes. So, negligible quantity of NO\textsubscript{x} and SO\textsubscript{x} would be generated during activation process.
Optimization of parameters for preparation of AC:

- DoE suggested quadratic model and two factor interaction model for the MB uptake and % Yield response, respectively. The correlation coefficients ($R^2$) values between experimental and predicted data were greater than 0.9 which was desirable. The lower CV (coefficient of variance) values and p-values of both models confirmed their validity.
- For MB uptake, the activation temperature was the significant parameter followed by impregnation ratio. The effect of holding time was less. The increase in activation temperature entailed formation and amplification of the pores, which improved the MB uptake. Besides, increase in temperature also caused CO$_2$ and the surface metal complex formed during activation with KOH to further gasify the carbon, leading to widening of micropore to mesopore. As chemical impregnation ratio increased, the catalytic oxidation also caused the widening of micropore to mesopore, therefore increasing MB uptake.
- For % yield, the activation temperature and holding time were significant parameters. The increase in temperature was bound to release volatiles as a result of intensifying dehydration and elimination reaction and also had the tendency to increase the C–KOH and C–CO$_2$ reaction rate, there by resulting in higher carbon burn-off and decreasing yield.
- As optimized preparation condition (which was model predicted value), the % yield of prepared ACs was in between 14.89 % to 17.2 %. The yield of CFAC (AC from empty cotton boll) was maximum i.e. 17.2 %.
- The value of MB uptake was also high for CFAC (AC prepared from empty cotton boll) i.e. 334.54 mg/L compared to MHAC (AC prepared from millet cob husk) and MAC (AC prepared from mustard husk) which were 298.15 and 317.54 mg/L, respectively.

Batch adsorption study of MB and RO84 on prepared ACs:

- We examined the effect of pH on the adsorption of dyes with pH ranges between 2 to 12. MB adsorption increased with increasing pH for all three prepared AC. RO84 adsorption increased with decreasing pH from 12 to 4. Then further decreasing pH of solution, no significant change in adsorption. This was visible probably due to presence of positively charged functional groups which could have conversely exerted strong electrostatic attractions with the anionic RO84 dye molecules.
• It was observed from the study that the % removal of both dyes decreased with increase in initial concentration. In principle, the initial dye concentration provided the necessary driving force to overcome the resistance to the mass transfer of dyes between aqueous phase and the solid phase of AC. The increase in initial dye concentration also enhanced the interaction between dye molecules and adsorbent. Therefore, an increase in initial concentration of dye enhanced the adsorption uptake of dye.

• We observed that the adsorption of both dyes were rapid in the initial stages and up to the first 120 min of contact time. After the 120 min, the removal efficiency reached equilibrium and quasi stabilized at a maximum value of ca. 98 %. In the adsorption process, initially dye molecules quickly reached the boundary layer by mass transfer and then they slowly diffused onto the adsorbent surface. It was observed that increasing the dosage of adsorbent gave more adsorption of both dyes onto ACs. The dye removal efficiency improved with increasing dosage of AC but equilibrium adsorption capacity of ACs decreased.

• The adsorption isotherm data of both dyes were best fitted in the Langmuir isotherm. The \(R^2\) value was greater than 0.98 at optimum condition of the ACs. Langmuir fitness to the adsorption process indicated that the dye molecules from bulk solution were adsorbed on specific monolayer which was homogeneous in nature. Separation factor (\(R_L\)) values were found < 1, which further confirmed that the Langmuir model was favorable. The maximum adsorption capacity found for MB onto MHAC, CFAC and MAC was 268.25, 298.34, and 280.45 mg/g, respectively. The maximum adsorption capacity found for RO84 onto MHAC, CFAC and MAC was 184.26, 208.12, and 189.32 mg/g, respectively.

• The statistical parameters and adsorption capacity results suggested that the pseudo-second-order adsorption model was a better equation to represent the adsorption kinetics of both dyes onto ACs. It indicated that the adsorption was carried out by multi-step process which involved adsorption on the external surface and then diffusion into the interior of adsorbent.

• Adsorption thermodynamics study indicated that the adsorption of MB and RO84 dyes endothermic and spontaneous in nature.
The spent AC was regenerated using 1N to 5N NaOH solution. After five adsorption-desorption cycle, 85 % MB and 76 % RO84 were absorbed by regenerated AC of empty cotton boll.

**Fixed bed column adsorption study for RO84 on CFAC:**

- In this study, we examined the effect of three different parameters like influent flowrate (10 to 18 mL/min), initial dye concentration (100 to 200 mg/L) and bed height (3 to 7 cm) for the removal of RO84.

- The breakthrough time reduced from 240 min to 64 min when flowrate was changed from 10 to 18 mL/min. The dye removal % decreased from 30 to 25 % and mass transfer zone was also decreased from 0.97 to 0.52 cm. With the increasing velocity, the rate of mass transfer increased which improved the rate of adsorption. Therefore, an early breakthrough was observed at higher flowrate. Also, higher flowrate reduced contact time between adsorbate and adsorbent, so an intra-particle diffusion phenomenon between dye molecules and AC was not favorable.

- The breakthrough time reduced from 240 to 30 min when initial concentration of RO84 was varied from 100 to 200 mg/L. The dye removal % increased from 27 to 35 % but mass transfer zone decreased from 1.09 to 0.22 cm. At high initial concentration, the vacant site was rapidly filled by dye molecules which led to decreased breakthrough time. High concentration gradient developed due to increasing initial dye concentration which resulted in increased dye removal %.

- The breakthrough time increased from the 55 to 200 min when the bed height was varied from 3 to 7 cm. The dye removal % increased from 22 to 34 % and mass transfer zone also increased from 0.33 to 1.25 cm. At lower value of bed height, the quantity of AC in the column was less, so there was less capacity for bed to adsorb dye from solution. Therefore, rate of adsorption increased faster. As the quantity of loaded adsorbent in column was high, the contact time between adsorbate-adsorbent enhanced resulting in better “sweep efficiency”. With increasing bed height, the enhancement of binding sites for adsorption of dye was probably more.

- There were four different kinetic models (i.e. Adam-Bohart, Thomas, Yoon-Nelson and Bed Depth Service Time (BDST)) applied to evaluate kinetic parameters and in order to evaluate the most suitable model for present fixed bed adsorption column. Thomas model
was better fitted for experimental data, based on $R^2$ value and minimum error values. However, the $R^2$ value was also high for Yoon-Nelson model but calculated and experimental time required for 50% breakthrough was highly deviated. $R^2$ was obtained $> 0.99$ in BDST model which suggested suitability of this model for the prediction of breakthrough curve.

**Batch adsorption optimization study of % MB and % RO84 removal by CFAC:**

- Adsorption process mostly depends on the pH, adsorbent dosage, initial dye concentration, temperature and time. The characteristics of effluent is not same for all industries, so study of above mentioned parameters using OFAT method is not enough to find optimum solution. Therefore, multi-level optimization technique was used to optimize the parameters simultaneously.
- The effect of individual parameters and interaction of two parameters on % removal of the two industrially very common dyes from effluent stream was observed.
- Desirability function was used to find out best optimum condition for % dye removal based on importance of each parameter.

**Conclusion and future scope:**

This study affirms that the locally, freely and amply available agro-wastes (i.e. millet cob husk, empty cotton boll and mustard husk) can be an appropriate option of non-renewable source based AC. The AC preparation conditions (i.e. activation temperature, impregnation ratio, and holding time) were successfully optimized using a three-factor CCD. At optimized preparation conditions, the values of both responses slightly deviated compared to predicted values which gave conformation of the suitability of the model.

As per the batch adsorption study, neutral or alkaline pH was favorable for the removal of MB while acidic pH was favorable for the removal of RO84 dye by prepared AC. The dye removal percentage increased by increasing dosage of adsorbent but the value of dye equilibrium adsorption capacity was reduced. Equilibrium adsorption capacity increased by increasing initial dye concentration. Equilibrium data were fitted well in the Langmuir isotherm model which confirmed that the sorption was homogeneous and occurred through physico-chemical interactions. The rate of adsorption was found to obey pseudo-second order kinetics with a good
correlation coefficient. The regeneration of spent AC study showed that there was no significant change in adsorption of dyes, but it slightly decreased with each cycle of AC regeneration. The negative $\Delta G^\circ$ values indicated that adsorption of dyes onto AC was feasible and spontaneous. The positive $\Delta H^\circ$ value depicted endothermic nature of the sorption. The techno-economic analysis showed that cost of AC can be produced by this method was less by 25% compared to the cost of commercial AC. From the analysis, it could be seen that the cost depends on the size of the manufacturing plant as well as on local regional regulation and availability of agro-wastes.

As per the fixed bed adsorption column experimental results, the adsorption of dye was dependent on the flowrate, influent RO84 dye concentration and the bed height. The time of breakthrough decreased with increasing flowrate as well as initial concentration of dye but it increased with increasing bed height. The dye removal percentage increased with increasing initial concentration and bed height but it decreased with increasing flowrate. Column kinetic data was well described by Thomas model and BDST model.

Modeling of MB and RO84 dye adsorption on AC by using CCD revealed that including all the main factors some interactions such as pH * concentration of dye, pH * dosage of an adsorbent, pH * temperature, concentration of dye * adsorbent dosage and concentration of dye * temperature significantly influenced the removal of both dyes from aqueous phase.

**Future Scope:**
- More investigation can be carried out with the basis of this work as background to prepare ACs with even better surface characteristics by surface modification.
- The choice of precursor and method of production of AC are important factors for process economy. Hence more comparative studies can be carried out with respect to precursor and method of production.
- Utilization of AC for other application other than wastewater treatment.
- Imparting functionality in AC for novel application which is of industrial advantage like silver impregnated AC to inhibit the growth of bacteria.

**List of Publications:**


**Patent:**


**References:**


