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Abstract:

The Sieved biomass of Ailanthus excelsa was chemically treated with Sulphuric acid (H₂SO₄) to produce acid- factionalized biosorbent used for O-Nitro Phenol removal from aqueous environment. Various analytical techniques were utilized to investigate the surface area, surface morphology, crystallinity, elemental composition of the sulphuric acid-treated biomass for removal of O-Nitro Phenol. Batch experiments were carried out as functions of different process parameters such as pH, initial dye concentration, biosorbent dose and temperature. The optimum conditions for removal of ONP were found to be pH (2.0), biosorbent dose (50 mg) and initial dye concentration (100 mg L⁻¹). The temperature (288K) had a strong influence on the biosorption process. The Langmuir, Freundlich and Temkin isotherms model, sorption of ONP onto SBAE were studied. The rate of sorption was found to obey pseudo-second order kinetics and intraparticle diffusion model with correlation coefficient value R² is 0.9981. Thermodynamic studies showed that the biosorption process was spontaneous and exothermic. The sieved SBAE is a promising biosorbent for ONP removal from aqueous solutions.

Keywords: Sulphonated Biomass of Ailanthus excelsa (SBAE), O-Nitro Phenol (ONP), Isotherm study.

1. INTRODUCTION

Phenols are widely used for the commercial production of a wide variety of resins including phenolic resins, which are used as construction materials for automobiles and appliances, epoxy resins and adhesives and polyamide for various applications [1]. Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential harm to human health. The US Environmental Protection Agency (EPA) regulations call for lowering phenol content in the wastewater to less than 1 mg/L [2]. The ingestion of such contaminated water in the human body causes protein degeneration, tissue erosion and paralysis of the central nervous system and also damages the kidney, liver and pancreas [3]. Therefore, it is considered necessary to remove the phenol from industrial effluents’ before discharging into the water stream. There are many methods such as oxidation, precipitation, ion change, solvent extraction and adsorption for removing phenols and its derivatives from aqueous solutions [4, 5]. The treatment of wastewater with activated
carbon is considered to be an effective method for the removal of phenol from waste solution because of its large surface area, micro-porous nature, high adsorption capacity, high purity and easy availability. However, the use of effective commercial activated carbons based on relatively expensive starting materials (wood or coal) is unjustified for most pollution control applications. It is, therefore, very important to examine the feasibility of using cheaper raw materials to prepare activated carbon. Many reports have appeared on the development of activated carbon from cheaper and readily available materials. Activated carbons have been prepared from corncob [6], sugar beet bagasse [7], apricot shell [8], sunflower seed hull [9], agricultural waste material [10], bagasses [11], rubber seed coat [12], coconut shell [13], apricot stone shells [14], oil palm fibre [15], bamboo [16], coconut husk [17] and Hevea brasiliensis seed coat [18]. To produce a value-added product from Ailanthus excelsa, it is proposed to convert it to activated carbon. In our previous study, activated carbon derived from Ailanthus excelsa showed remarkable efficiency for the removal of basic dye from aqueous solution [19]. The phenolic compounds are known by their carcinogenicity and high toxicity as well as creating unpleasant taste and odour in water resources. The present study develops a cost-effective technology for the treatment of water contaminated with phenolic compounds, including Phenol (Ph), 2-chlorophenol (2-CP), and 4-chlorophenol (4-CP). So, two sorbents, rice bran ash (RBA) and biomass of brown algae, Cystoseiraindica, were used and results were compared with the commercially granular activated carbon (GAC) [20]. Environmental pollution, especially organic pollutants, represents an essential threat to human health and natural ecosystems globally (Ali, 2018; Chatterjee and Dasgupta, 2005; Elsagh et al., 2017). In this work, the suitability of the sulphonated activated carbon prepared from the Ailanthus excelsa for ONP adsorption was assessed. The equilibrium and kinetic data of the adsorption were then studied to understand the adsorption process.

2. EXPERIMENTAL
2.1 Materials and Methods
Analytical-reagent grade o-nitrophenol was used as the adsorbate in adsorption. A stock solution was prepared by dissolving the required amount of phenol in double distilled water. Working solutions of the 25 to 100 mg/L concentrations were prepared by successive dilutions.

2.2.1 Preparation of sulphonated biomass of Ailanthus excelsa:

Preparation of Ailanthus excelsa plant (Sulphonated biomass), commonly known as tree of heaven is a large delicious tree found in Himachal Pradesh, Chhattisgarh and Western Ghats of Maharashtra state in India. The biomass Ailanthus excelsa was collected from the locally available garden. The stalks of Ailanthus excels were dried, washed with distilled water to remove adhered impurities from its surface. The dried biomass was crushed, milled and sieved to 100µm particle size. The dried biomass was soaked with Conc. H2SO4 for period of 6 h and the resulting reaction mixture was kept overnight in fume hood. The reaction mixture was repeatedly washed with cold water till to complete remove acid and filtered to obtain Sulphonated carbon. This is then dried in oven at 100°C time for 12 hr. The resulting Sulphonated carbon of Ailanthus excels was preserved and used as an adsorbent for ONP removal. ONP concentration determined by the Beer-Lambert law. The ONP Absorbance measured at 270 nm on UV-Visible spectrophotometer.
2.2.2 Batch equilibrium and kinetic studies

In adsorption equilibrium, experiments were conducted in a set of 250 mL Erlenmeyer flasks, where solutions of phenol (25 mL) with different initial concentrations (25–100 mg/L) were added in these flasks. Equal masses of SBAE of particle size 100 µm were added to phenol solutions and each sample was kept in an isothermal shaker of 120 rpm at 25 °C for 2 h to reach equilibrium of solution mixture. The pH of the solution was not adjusted initially. A similar procedure was followed for another set of Erlenmeyer flask containing the same ONP concentration without activated biomass to be used as a blank. The flasks were then removed from the shaker and the final concentration of phenol in the solution was analyzed using a double beam UV–visible spectrophotometer at 270 nm wavelength. The samples were filtered prior to analysis in order to minimize interference with the analysis. Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium, \( q_e \) (mg/g), was calculated by

\[
q_e = \frac{(C_0 - C_e)}{m} \ldots (1)
\]

\[
\% \text{ Removal} = \frac{C_i - C_e}{C_i} \ldots (2)
\]

Where, \( C_0 \) and \( C_e \) (mg/L) are the liquid-phase concentrations of ONP at initial and equilibrium, respectively. \( V \) (L) is the volume of the solution, and \( W \) (g) is the mass of dry adsorbent used. The procedures of kinetic experiments were basically identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of phenol were similarly measured.

3. RESULTS AND DISCUSSION

To design effective and user-friendly adsorption model it was considered necessary to carry out adsorption with a kinetic view point and effects of contact time, initial ONP concentration, pH and temperature on the uptake rate of the ONP was monitored very carefully.

3.1 Effect of Material dose and contact time:

Effect of biosorbent dose on biosorption of ONP by SBAE was investigated. The amount of biosorbent was varied from 25 to 100mg in 25 mL ONP solution, while all the other such as pH, contact time and temperature were kept constant. Data obtained from the experiments are presented in Figure.1. With increase in biosorbent dose from 25mg to 400 mg, the ONP removal efficiency increases from 10.32% to 61.81 %, which is probably due to an increase in the Number of binding sites available for biosorption further increase in biosorbent dose reduces the percentage removal.

Figure-1 Effect of Biomass dose.
3.2 Effect of Contact Time:
The effect of contact time on the removal of ONP is shown in Figure-2 and about 63.81% dye removal takes place in 2 hours by Sulphonated biomass. The changes in the rate of adsorption might be due to the fact that initially all the adsorbent sites are vacant and solute concentration gradient is very high. Later, the lower adsorption rate is due to a decrease in ONP of vacant sites of adsorbent and phenol concentrations. The decreased adsorption rate, particularly, toward the end of experiments, indicates the possible monolayer formation of ONP on the adsorbent surface.

**Figure-2 Effect of contact time on ONP removal**

![Graph showing the effect of contact time on ONP removal.](image)

3.3 Effect of initial dye concentration:
Biosorption of ONP onto SBAE was also carried out at different initial dye concentrations (25, 50, 75, and 100 mg L\(^{-1}\)) and the results are shown in Figure 4. It is clearly evident from the figure that the biosorption capacity increases with increasing initial ONP concentration. Initial ONP concentration provides an important driving force to overcome all mass transfer resistances of all molecules between the aqueous and solid phases. Hence, a higher initial ONP concentration of ONP will enhance the biosorption process.

**Figure-4 Effect of Concentration on ONP Removal**

![Graph showing the effect of concentration on ONP removal.](image)
3.4 Effect of pH:
Solution pH is an important monitoring parameter influencing the sorption behavior of adsorbate onto biosorbent surface due to its impact on both the surface binding-sites of the biosorbent and the ONP solution. In the present study, the effect of pH on biosorption of ONP onto SBAE was studied over a pH range of 2–10. Results are shown in Figure-5. The amount of phenol removal at equilibrium decreases with increasing pH, appreciably up to pH 2.0. With further increase in pH, there is no significant increase in the amount of phenol removed. Maximum removal is observed at pH 2.0. The pH of the aqueous solution affects both the surface charge of the biosorbent material as well as the degree of ionization of the phenol molecule.

Figure-5 Effect of pH on ONP removal.

3.5 Effect of Temperature:
Temperature has pronounced effect on the sorption removal of ONP from aqueous solutions. As such, the effect of temperature on the biosorption process of ONP was studied in the range of 288 to 318 K and the results are depicted in Figure 5. The figure shows that the phenol uptake capacity decreases with increasing temperature. This finding suggests that ONP uptake process was exothermic in nature. The negative correlation between temperature and ONP biosorption capacity may be due to the weakening of bonds between the ONP molecules and the active site of the biosorbent. Also with increasing temperature, the solubility of ONP increases. Consequently, the interaction forces between the solute and the solvent are stronger than those between the solute and the biosorbent. As a result, the solute is more difficult to adsorb.

Figure-6 Effect of temperature on ONP removal.
3.6 Adsorption Kinetics:

Adsorption is a physiochemical process that involves the mass transfer of a solute (adsorbate) from the fluid phase to the adsorbent surface. A study of kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for efficiency of the process. The applicability of the pseudo-first-order and pseudo-second-order model was tested for the adsorption of ONP onto Sulphonated biomass. The best-fit model was selected based on the linear regression correlation coefficient, R² values. If the second-order kinetics is applicable, then the plot of t/qt vs. t (Figure.7) and Figure.8 log (qe-qt) vs. T should show linear relationship.

Fig.7 Plot t/qt vs. T

![Plot t/qt vs. T](image1)

Figure.8 log (qe-qt) vs. T

![Log (qe-qt) vs. T](image2)
Figure-9 Kinetics of Adsorption

Table- 1 Kinetic and thermodynamic parameters for the sorption of ONP onto Sulphonated biomass of Ailanthus excelsa. Pseudo first order and Pseudo second order model

<table>
<thead>
<tr>
<th>Model</th>
<th>qe (mg/g)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo first order model</td>
<td>0.2528</td>
<td>0.6388</td>
</tr>
<tr>
<td>k1 (min⁻¹)</td>
<td>-0.005</td>
<td></td>
</tr>
<tr>
<td>Pseudo second order model</td>
<td>10.7526</td>
<td>0.9790</td>
</tr>
<tr>
<td>k2 (g/(mg min)) =9.4020x10⁻³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intraparticle diffusion model</td>
<td>C (mg/g)</td>
<td>0.9981</td>
</tr>
<tr>
<td>kd (mg/g min)</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td>kd=0.9603</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermodynamic parameter</td>
<td>ΔS° (J/mol K)</td>
<td>ΔG° (kJ/mol)</td>
</tr>
<tr>
<td>ΔH° (kJ/mol)</td>
<td>636.1197</td>
<td>-3145.565</td>
</tr>
<tr>
<td>ΔH° = -2.2131</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Kinetics and thermodynamics of ONP sorption on SBAE. The intraparticle diffusion equation is expressed as follows,

\[ q_t = K_d \ t^{1/2} + C \]  \hspace{1cm} (3)

Where, kd is the intraparticle diffusion rate constant (mg/g min1/2). The data for intraparticle diffusion are given in Table-1. The linear portion of the plot does not pass through origin. This deviation from the origin may be due to the variation of mass transfer in the initial and final stages of the adsorption process. This confirms that the adsorption of ONP on of Ailanthus excelsa plant was a multi-step process involving adsorption on the external surface and diffusion into the interior.

3.7 Thermodynamics of Adsorption Process.

Thermodynamic parameters evaluated for ONP adsorption onto SBAE are the free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°). These parameters were calculated using the following equation.

\[ \Delta G^° = -2.303 \ RT \log K_d \]  \hspace{1cm} (4)

Where qe is ONP concentration at equilibrium onto SBAE (mg/L), R is universal gas constant (8.314 J/mol K), and Ce is ONP concentration at equilibrium in solution (mg/L). The values of ΔH° and ΔS° were determined from the slope and intercept of the plot of ln KD versus 1/T. Gibbs free energy. Change of sorption (ΔG°) was
calculated using Eq. (4). The adsorption of ONP increases rapidly with a decrease in temperature. The increase in adsorption capacity of SBAE was attributed to the enlargement of pore size and activation of the sorbent surface with temperature. The results also indicated that the adsorption of ONP is an exothermic process. Thermodynamic parameters ($\Delta H^0$, $\Delta S^0$ and $\Delta G^0$) for ONP. Adsorption was evaluated using Eqs. (3 and 4). The values of $\Delta H^0$ and $\Delta S^0$ were determined from the slope and intercept of the plot of ln Kd versus 1/T. Table -1 show the thermodynamic parameters for ONP adsorption of SBAE. The calculated values of $\Delta H^0$, $\Delta S^0$ and $\Delta G^0$ were found to be -2.2131kJ/mol$^{-1}$ + 636.1197 KJ/mol$^{-1}$ and -3145.565 KJ mol$^{-1}$ respectively. The negative value of $\Delta H^0$ (-2.2131kJ/mol$^{-1}$) indicates that the adsorption of ONP onto of SBAE is an exothermic reaction. The calculated value of $\Delta G^0$ (-3145.565 KJ mol$^{-1}$) indicates spontaneous nature of the adsorption process. Further the positive value of entropy change, $\Delta S^0$ reflects the affinity of SBAE for ONP.

Figure.9 Plot of Ln KD vs. 1/T

3.8 Adsorption Isotherm Study:

3.8.1 Langmuir Isotherm

The Langmuir (1916) sorption isotherm is applied to equilibrium sorption assuming monolayer sorption onto a surface with a finite Number of identical sites constitution and fundamental properties of solids and liquids. The Langmuir equation is written as

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{KLq_mC_e}$$

The shape of this isotherm can also be expressed in terms of separation factor (RL), which is given as follows: Where KL is Langmuir constant (L/mg) related to the affinity of binding sites and the free energy of sorption. $q_e$ is ONP concentration at equilibrium onto biosorbent (mg/g). $C_e$ is ONP concentration at equilibrium in solution (mg/l). $q_m$ is ONP concentration when monolayer formation biosorbent (mg/g) on SBAE.
3.8.2 Freundlich Isotherm

The mathematical equation for heterogeneous surface energy systems shown by Freundlich is given by:

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \]  
(6)

The \( K_F \) and \( n \) are Freundlich constants, determined from the Plot of \( \ln q_e \) versus \( \ln C_e \). The parameters \( K_F \) and \( 1/n \) are related to sorption capacity and the sorption intensity of the system. The magnitude of the term \( (1/n) \) gives an indication of the favorability of the sorbent/adsorbate systems.

3.8.3. Tempkin Isotherm.

The linearized Tempkin equation is given by the following equation

\[ q_e = \beta \ln x + \beta \ln C_e \]  
(7)

Where, \( \beta = \frac{RT}{b} \), \( T \) is the absolute temperature in Kelvin, \( R \) is the universal gas constant (8.314 J/mol K), and \( b \) is the Tempkin constant related to heat of sorption (J/mg). The Tempkin constants \( a \) and \( b \) are calculated from the slope and intercept of \( q_e \) versus \( \ln C_e \).
Figure-12 Plot of ln $q_e$ vs. ln $C_e$

Table -2 Results of various isotherm plots for the adsorption of ONP onto Sulphonated Biomass of Ailanthus excelsa (SBAE).

<table>
<thead>
<tr>
<th>Models</th>
<th>Isotherm constants</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_m$(mg/g) 0.0603, $K_L$(L/mg) -91.491</td>
<td>0.9491</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$n$ =0.4310, $K_F$(mg/g) 9.7723×10^{-8}</td>
<td>0.9824</td>
</tr>
<tr>
<td>Temkin</td>
<td>$(l/g)$ -216936.53, $K_T$(mg/l) 0.0386</td>
<td>0.9234</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

The prepared material of Sulphonated Biomass of Ailanthus excelsa (SBAE) was subjected to extensive characterizations using a variety of techniques such as scanning electron microscope coupled with energy-dispersive X-ray spectroscopy (SEM/EDX), X-ray diffraction (XRD) method. The operating conditions were optimized to improve the adsorption process efficiently. Batch experiments were carried out as functions of different process parameters such as pH, initial dye concentration, biosorbent dose and temperature. The optimum conditions for removal of ONP were found to be pH (2.0), biosorbent dose (50 mg), and initial dye concentration (100 mg L$^{-1}$). The temperature (288K) had a strong influence on the biosorption process. The Langmuir, Freundlich and Temkin isotherms model, biosorption of ONP onto SBAE were studied. Thermodynamic studies showed that the biosorption process was spontaneous and exothermic. In this work of SBAE shows promising adsorption capacity for ONP removal. The maximum sorption for ONP solution concentration 100mg/l/25ml, sorbent dosage (50mg/25 ml), contact time (120 min) and temperature (288 K) were observed. The maximum removal of ONP was attained at pH 2.0. The equilibrium data were fitted well in the Langmuir, Freundlich and Temkin isotherm models which confirmed that the sorption is heterogeneous and occurred through physico–chemical interactions. The rate of sorption was found to obey pseudo-second order kinetics and intraparticle diffusion model with correlation coefficient value $R^2$ is 0.9981. The negative $\Delta G^\circ$ values indicated that the sorption of dye onto biosorbert was feasible and spontaneous. The negative $\Delta H^0$ value depicted exothermic nature of the sorption. The parameters KF and n (Table-2) indicated the sorption capacity and the sorption intensity of the system.
5. ACKNOWLEDGEMENTS

I am thankful to Dr. A.A. Kale sincerely thankful to Head department of chemistry Prof. A.B. Nikumbh and Principal Dr. K.G. Kanade for providing infrastructural facility to complete my research work.

6. REFERENCES.

