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COMPARISON OF BIOMASSES AND STUDY OF ACACIA NILOTICA BRANCHES AS AN ADSORBENT MATERIAL FOR PHENOL REMOVAL

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ABSTRACT

A vast amount of biomass is produced by India in the form of waste products from agriculture and forests. To solve the problem of waste disposal, they need to be put to good use. As a carbon source, biomass can be used to make low-cost phenol adsorbents. Three biomasses were chosen for investigation: the *Acacia nilotica* branches (AC), the Lantana camera (LA) and the rice husk (RI). Because the amount of phenol removed by these biomasses was small, they had to be activated through a thermochemical process. As a result, their characteristics as adsorbents improved tremendously. They were named activated AC (ACC), LA (LAC), and RI (RIC). The percentage removal of phenol by these adsorbents improved dramatically. Phenol removal by ACC was highest with a value of 97% removal. Further adsorption studies were focused on ACC. Scanning electron microstructure studies were applied to observe the change in the structure of the adsorbent after activation. Fourier transform infrared analysis showed the significant adsorption of phenol on the adsorbent. Langmuir, Freundlich and Temkin models were used to examine the mechanism of the adsorption process.

Keywords: Acacia nilotica branches, activated char, adsorption, biomasses, phenol.

1. INTRODUCTION

A large number of biomasses are produced every year [1, 2]. Farmers are seen burning them as a solution to clearing and preparing the fields for the next crop. However, the process generates greenhouse gases. Moreover, biomasses have a high moisture content and low bulk density, making them difficult to transport from one place to another. So it is mandatory to investigate various possible ways to utilise them at the exact location as its production [3].

The literature review accounts for various biomasses applications as adsorbents for removing organic compounds, especially phenols in industrial effluents [4–8]. In this work, three biomasses, *Acacia nilotica* branches (AC), *Lantana camera* (LA) and rice husk (RI), have been considered to be studied (based on their availability) for the removal of phenol. The presence of phenol in water streams affects the food chain. The pollutant finds its way to water sources mainly through the effluents from paint, pesticides, coal conversion, polymeric resin, petroleum and petrochemicals industries [9]. Therefore, phenol is listed as a high-priority chemical in various databases [10].

Three biomasses, namely AC, LA and RI, were analysed for their suitability as adsorbents. Proximate analyses [ash, fixed carbon (FC) and volatile matter (VM)] and bulk densities were determined following American Society for Testing and Materials (ASTM) standards. AC, LA and RI were subject to phenol sequestration from aqueous solutions.

The percentage of phenol removed by AC, LA and RI from a 1 g/l aqueous solution is relatively low. Adsorbent AC has been shown to remove up to the maximum value of 35% of its contaminant. In addition, adsorbents reveal substantially lower Brunauer-Emmett-Teller (BET) surface area, FC and high VM than commercial-grade carbon intended for phenol's adsorption.

The surface area of commercial-grade carbon ranges from 450 to 1500 m^2/g (actual area available to adsorbate may be much less than the total) [11, 12]. Thermochemical treatment

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methods have been widely documented to activate biomasses by increasing the carbon percentage and porousness of the material [12–14]. ACC, LAC and RIC are the activated biomasses. Therefore, ACC was chosen for further adsorption research based on the comparison. The morphological alteration in the surface of adsorbents was confirmed by scanning electron microstructure (SEM) examination.

The activated carbon ACC underwent a study of the effects of the dose of adsorbents, slurry pH, initial phenol concentration, the slurry agitation speed and contact time of the phenol solution on the adsorbents. The parameters were examined independently to optimise the operational parameters for generating adsorption isotherms. The adsorption isotherm was analysed mathematically using Langmuir, Freundlich and Temkin models.

Based on phenol removal percentages over time, kinetic studies were conducted, and the adsorption process for ACC was examined using pseudo-first- and pseudo-second-order kinetics. In addition, Fourier transform infrared (FTIR) analysis was completed to confirm the adsorption of phenol. Therefore, it was possible to create an adsorbent (based on available biomasses) with high BET surface area, which was comparable to commercial-grade carbon. The adsorbent could remove a great percentage of phenol from aqueous solutions. It was also possible to regenerate the adsorbent.

2. MATERIALS AND METHODS

Various experiments were conducted for the present work. Details are mentioned in the following subsections.

2.1 Preliminary study of biomasses

Biomasses were analysed in bulk densities and proximate analysis as per standard methods and ASTM: D3173-75. To calculate the biomass volume, one must consider particle volume, interparticle void volume and the particle's interior pore volume. They were also tested for moisture, VM, FC and ash percentages. Standard protocols for raw material storage and processing were used to determine biomass bulk densities [11].

2.2. Preparation of adsorbents

Biomasses AN, LA and RI were separately acquired, washed and ground in powder form, passing a 300-micron screen. The samples were treated with 30% H_3PO_4 for 3 hours at 37°C. The resulting slurry was filtered, and the residue was washed thoroughly till a pH of 7 was obtained. The residues obtained were dried and pyrolysed at 500°C in the muffle furnace. The char was digested with NaOH solution (12%) for 5 hours at 68°C. The resulting solid particles were filtered out, washed and dried. The samples thus obtained were powdered and stored for further studies [15].

2.3. Characterisation of adsorbents

The phenol number (amount of phenol required by the adsorbent for 90 per cent phenol removal), pH of biomass slurries in water, iodine number and methylene blue number were used to characterise AC, ACC, LA, LAC, RI and RIC. The nitrogen adsorption method was used to determine the surface area of activated biomass (Quantachrome BET surface area analyser). A 'Laser Diffraction Particle Size Analyser' was used to determine the particle size of the adsorbents. The properties of the adsorbents under investigation are listed in Tables 2 and 3.

2.4. Adsorption experiments on adsorbent materials

Batch tests in conical flasks with 100 ml of phenol solution (1 g/l) were performed for the adsorption research [12, 14]. As mentioned in 2.3, AC, LA, RI and ACC were subject to adsorbent studies. The temperature of the study was set at 25°C. The effects of adsorbent dosage, pH, contact time, initial phenol content and shaker rpm on ACC were investigated. A spectrophotometer was used to determine the amounts of phenol in aqueous solutions. An investigation of the effects of adsorbent dose on the adsorption process was carried out. ACC of various quantities were equilibrated with phenol solutions for 24 hours at 200 rpm at 25°C. Investigation of the influence of pH requires the preparation of phenol solutions. The whole acid-base range was used with 0.1 NaOH and 0.1 H_2SO_4 while maintaining all other parameters constant. Except for the dosage effect, each investigation used a set optimum amount of adsorbents equilibrated with a phenol solution of 1 g/l. To investigate the influence of time on percentage phenol removal at 25°C, the adsorbent dosage, pH, initial phenol concentration and shaker rpm were all fixed using a phenol (1 g/l) solution. The extents of adsorption were examined for various periods till adsorption consistency was achieved. The amount of phenol adsorbed was determined using the formula shown as eqn (1)

$$q_e = (C_0 - C_e) . V/m \tag{1}$$

In eqn (1), q_e (mg/g) is the quantity of phenol adsorbed per unit mass of adsorbent, C_0 is the initial phenol concentration, C_e is the phenol concentration at equilibrium, V is the volume of solution and m is the mass of adsorbent added for each test.

2.5. SEM and FTIR studies on ACC

The adsorbent ACC selected for study was subjected to SEM analysis before and after the activation process on JEOL, JSM-6610LV.

The adsorbent ACC was further subjected to FTIR analysis on BRUKER TENSOR 27 before and after the adsorption.

2.6. Regeneration of adsorbents

The regeneration process was performed on ACC using 100 ml of 1 M NaOH solution [14]. 1.2 g of adsorbent was added to the conical flasks at 25°C and stirred at 200 rpm. The pH of slurries containing NaOH was kept at 6.5 for 5 hours. The extent of desorption of phenol was determined using a spectrophotometer. The equipment measured the concentrations of supernatant solutions (described in section 2.4). The adsorbents that had been regenerated were filtered out, thoroughly washed, dried and stored.

3. RESULTS AND DISCUSSIONS

Results of various experiments performed, as mentioned in the previous sections, are discussed under various subheads as follows:

3.1. Preliminary study of biomasses

Bulk densities and proximate analysis of biomasses were determined on AC, LA and RI as explained in section 2.1. The density of AC and LA were above 200.0 kg/m^3 (Table 1), leading to the fact that they could be economically transported with ease. However, the identical

Table 1: Proximate analysis of biomasses.

Biomass	**FC (%)**	**Ash (%)**	**VM (%)**	**Bulk density (kg/m^3)**
AC	25.00	2.50	72.50	210.0
LA	23.50	12.30	64.20	250.0
RI	20.00	18.00	62.00	110.0

value for RI is 110.0 kg/m^3, meaning it needs briquetting. Furthermore, all three biomasses considered had a considerably high FC percentage, a desired characteristic of adsorbents for phenol transfer. Also, VM and Ash percentages of all biomasses (except the ash content of 2.5% of AN) were high, making them more suitable to be considered adsorbent materials [12, 14].

3.2. Characterisation and adsorption study of biomasses as adsorbents

The biomasses, namely AC, LA and RI, were selected for the study as adsorbents. These biomasses were prepared in the form of powder (section 2.2). The resulting samples of AC, LA and RI were subject to various characterisations. The results indicate a reasonably higher value of iodine number of 485 for AC than LA and RI (Table 2). Values of BET surface area of biomasses are pretty low. Particle sizes of the materials are comparable to that of commercial-grade carbon [16]. Methylene blue values, which also indicate the adsorption power of materials, are shallow, with a value of AC as highest on 40 mg/g. In contrast, the same values for LA and RI are lower at 5.8 and 0.45, respectively. Therefore, the characterisation of selected biomass for their potential for adsorption of phenol is very poor. A meagre percentage of phenol removal confirms this fact for AC at 35%, LA at 17% and RI at 1% (Fig. 1). It suggests that they need to be activated to obtain better values of FC, BET surface area, iodine numbers and methylene value adsorption.

3.3. Characterisation of activated adsorbents

As explained in section 3.2, biomasses without activation had feeble adsorption capacities. Commercial-grade carbon (CGC) has an excellent affinity for phenol. It could be because CGC generally has a high FC value, BET surface area, iodine number and methylene blue adsorption. On the other hand, it has low values of ash and VM [17]. As mentioned in section 2.2, thermochemical treatment was given to all the biomasses. After comparison, ACC was confirmed as the best adsorbent [Table 3]. It has a BET surface area comparable to CGC [12, 18]. For further adsorption and kinetics, study ACC was selected.

SEM Studies on ACC: The surface morphologies of AC and ACC were investigated using JEOL JSM-6610LV, as explained in section 2.5. By comparing SEM micrographs (Fig. 2), it was confirmed that ACC has a porous and rough morphology, clearly justifying its high BET surface area of 450 m^2/g (Table 3).

3.4. Adsorption studies on ACC

For the generation of adsorption isotherms of ACC, various parameters affecting adsorption were optimised. The procedure concerning the matter is explained in section 2.4.

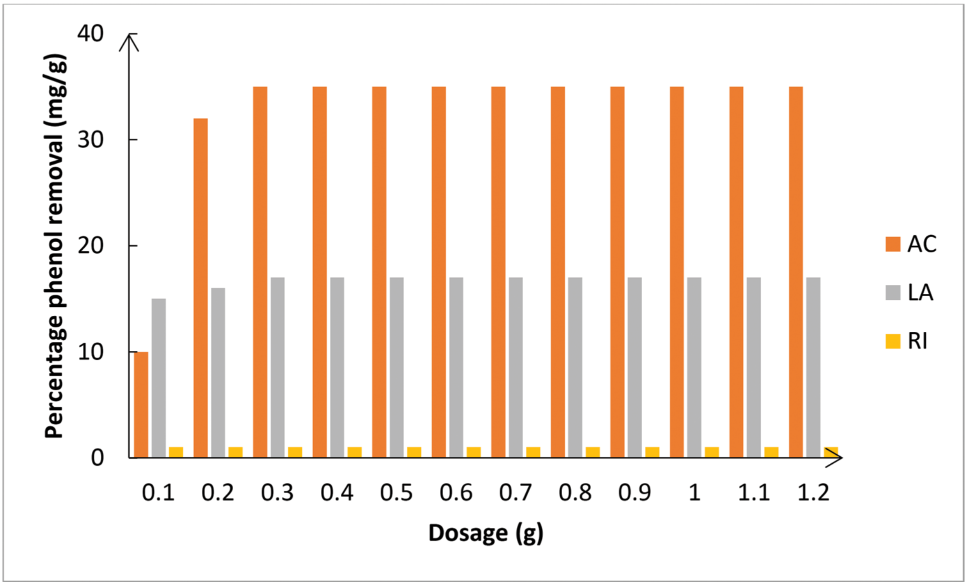


Figure 1: Percentage removal of phenol with the dosage of biomasses.

Table 2: Characterisation of biomasses as adsorbents.

Properties	AC	LA	RI
Ash content on a dry basis (%)	2.50	12.30	18
FC on a dry basis (%)	25.00	23.50	20
VM on a dry basis (%)	72.50	64.20	62
pH of slurry	-	-	-
Phenol number (g)	-	-	-
Iodine number	485	70.00	10.10
BET surface area (m^2g^{-1})	50	46.4	35.5
Particle size (μm)	300	180	300
Methylene blue adsorption (mg/g)	40	5.8	0.45

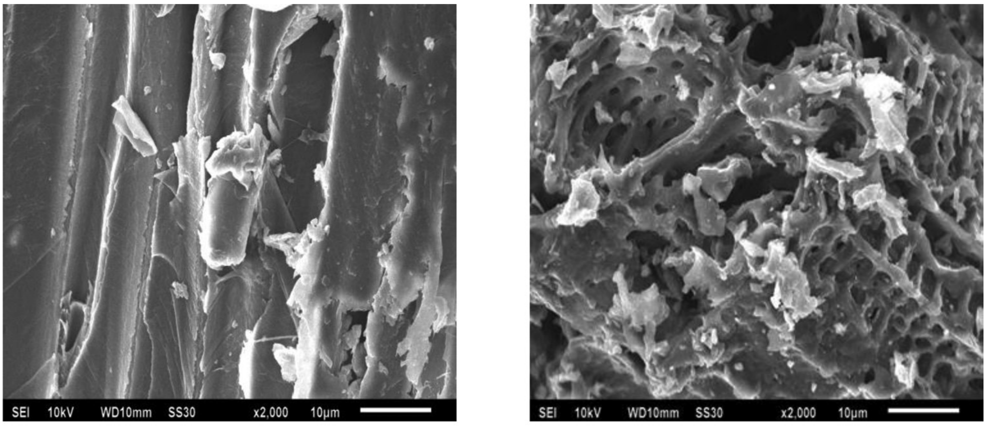
3.4.1 Adsorption effects of operating parameters

Selection of one set of best parameters for the adsorbate-adsorbent system requires investigating the effect of dosage, initial phenol concentration, agitation speed, contact time and pH of the adsorbate solution on the adsorption process [12]. They are discussed in the following order:

Effect of dosage on phenol adsorption on ACC: The study was conducted on ACC. To determine the effect of dosage on phenol adsorption, as described in section 2.4, Fig. 3 shows that the percentage removal of phenol increases with the number of dosages of activated biomass. For example, at 97% phenol removal with the adsorbent dosage of 1.2g for 100 ml of 1 g/l phenol solution, the amount of ACC required becomes constant.

Table 3: Characterisation of the activated biomasses chosen as adsorbents.

Properties	**ACC**	**LAC**	**RIC**
Ash content on a dry basis (%)	1.0	5.0	4.80
FC on a dry basis (%)	87.0	85.0	84.20
VM on a dry basis (%)	12.0	10.0	11.00
pH of slurry	6.5 (1.2%)	7.5 (1.0%)	6.8 (1.1%)
Phenol number (g)	0.8	1.0	-
Iodine number	870	325	750
BET surface area (m^2g^{-1})	450	151	301
Particle size (μm)	45	42.3	25.3
Methylene blue adsorption (mg/g)	155	50.1	55.5



(a) (b)

Figure 2: Scanning Electron Microstructure Analysis of (a) AC and (b) ACC.

Effect of slurry pH on phenol adsorption on activated biomass: As explained in section 2.4, the effect of pH on phenol adsorption on ACC was investigated. The maximum removal of phenol by the adsorbent occurs at a pH value of 6.5.

The effect of initial phenol concentration on adsorption of activated biomass: As explained in section 2.4, the effect of initial phenol concentration on phenol adsorption on ACC was investigated. It was discovered that the initial concentration of phenol does not affect the adsorption process. Regardless of initial phenol concentration, the maximum value for phenol removal for ACC was 97%.

The effect of slurry agitation on phenol adsorption on activated biomass: As explained in section 2.4, the effect of agitation was studied at 50, 100, 150, 200, 225 and 250 rpm for ACC. When a 4-hour contact time was maintained at a pH of 6.5 and a temperature of 25°C, the percentage removal of phenol increased to 97% at an agitation speed of 200 rpm (Fig. 4).

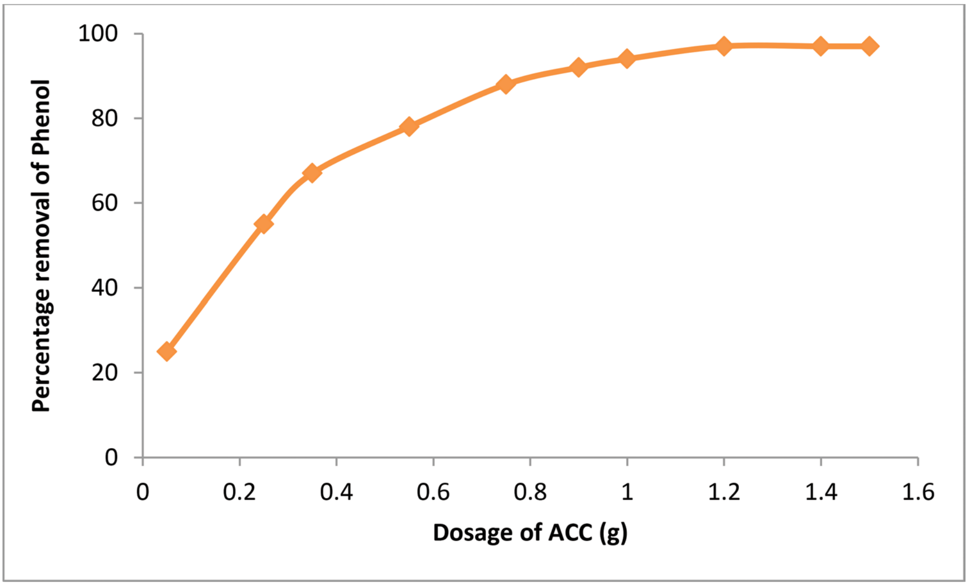


Figure 3: Variation of percentage phenol removal with the dosage of ACC.

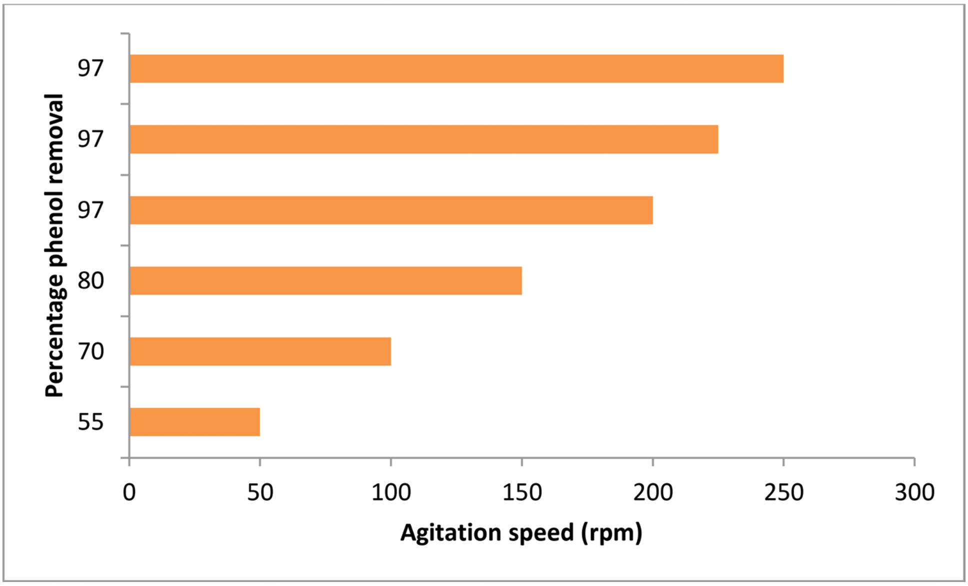


Figure 4: Effect of agitation speed on phenol removal.

The effect of time on adsorption: as discussed in section 2.4, time affected phenol removal by the adsorbent. Maximum phenol removal from 1 g/l of phenol solution takes 4 hours by ACC (Fig. 5). Thus, this research helped to determine the optimum time to conduct an adsorption study. In addition, the data collected in this study will be used for kinetic studies as explained in section 3.4.3.

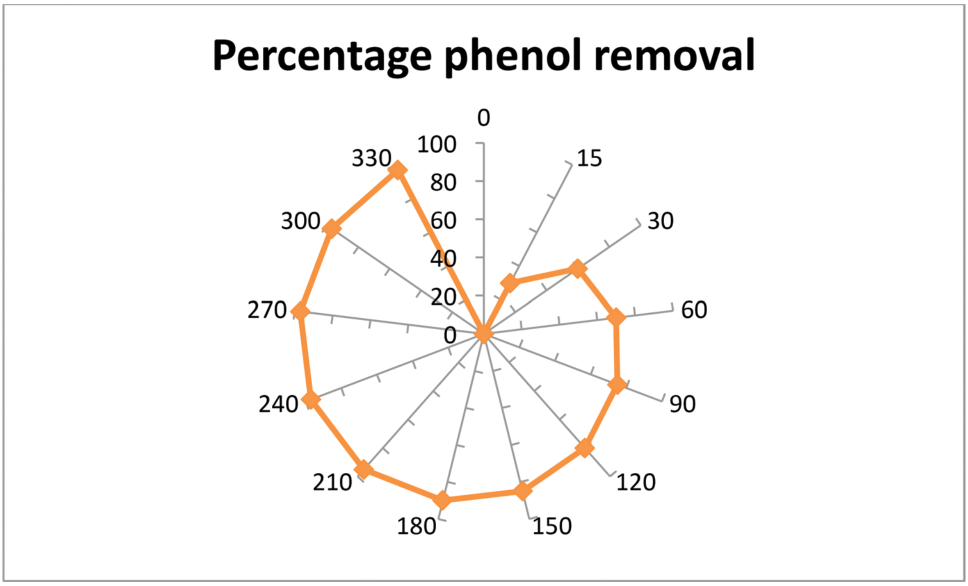


Figure 5: Effect of contact time on the percentage removal by ACC.

3.4.2 Adsorption isotherms of phenol as an adsorbate on the adsorbent

Based on a thorough examination of the effects of various parameters on adsorption, optimal conditions for adsorption studies on the adsorbent was established. Isotherm was generated at the temperature and volume of phenol solution used at 25°C for 100 ml. Figure 6 depicts the adsorption curve obtained.

The adsorption study for ACC ranges from 903 to 975 mg/l of phenol supernatant concentration (Ce). Thus, the adsorbent can adsorb up to 500 mg of phenol per gram of adsorbent [12]. Furthermore, the equilibrium data fit the well-known mathematical models developed by Langmuir, Freundlich and Temkin [19–21] as shown in Figure 7.

Adsorbate-adsorbent system in the entire concentrations range (from 903 to 945 mg/l) follows the Temkin isotherm [12]. The least square fit value (R^2) is 0.99. The value of A is 0.001 l/mg, and the value of b1 is 0.82 J/mol (Table 4).

3.4.3. Kinetics of adsorption of phenol on the adsorbent

First and second-order kinetics are used to study the kinetics of adsorption [12]. The data from Fig. 5 were used to calculate kinetic constants. The kinetic data of the activated biomass-adsorbent system was found to fit into first-order kinetics. The constant values for first-order kinetics are denoted by q_e, k_1 and R^2 [22]. Similarly, kinetic data also fits second-order kinetics with an R^2 value of 0.98. (Table 5). The constant values for second-order kinetics are denoted by q_e, h and R^2 [23].

3.5. FTIR studies on ACC

Based on functional groups visible in the FTIR spectral analysis of ACC before and after adsorption, various sites for adsorbate linkage to the adsorbent were observed. The spectrum of the adsorbent, before and after the adsorption of phenol (Fig. 8), revealed the presence

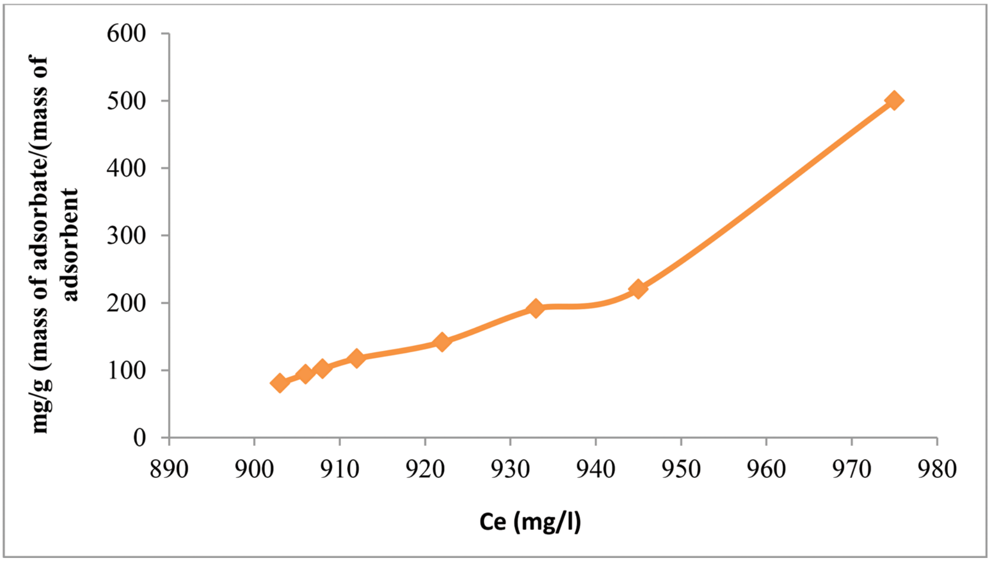
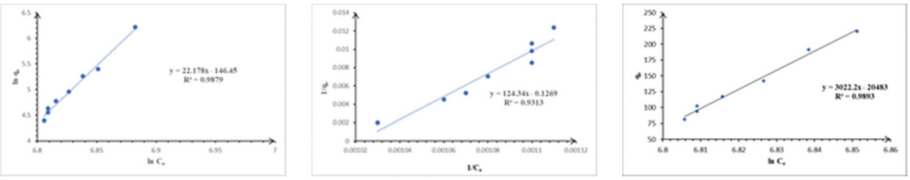


Figure 6: Adsorption curve for ACC with aqueous phenol solution as adsorbate.



(a) Freundlich (b) Langmuir (c) Temkin

Figure 7: Regression curves of Freundlich, Langmuir and Temkin models.

of aromatic, amino, carbonyl, carboxyl, cellulosic, chlorides and hydroxyl structures in the 4000–400cm^{-1} range [11]. A large band at 3468.15 cm^{-1} confirms the presence of the hydroxyl group on ACC after adsorption. The carboxylate region's weak peaks moved from 1560.48 cm^{-1} before adsorption to 1548.06 cm^{-1} after adsorption, indicating attachment of phenol to the adsorbent [4]. The FTIR images also show that a carbonyl-containing group is formed when AC is carbonised (activated). Therefore, it is reasonable to justify that phenol adsorption on ACC was possible through a 'donor–acceptor complex mechanism'. The Carbonyl group's oxygen atom and aromatic ring of the phenol molecule could have served as an electron donor and an electron acceptor.

3.6 Adsorbent regeneration

As mentioned in section 2.6, a regeneration test was performed on activated biomass in a single step. Ninety per cent of the phenol adsorbed on the used ACC could be recovered. Thus, the procedure aids in regenerating adsorbents to a large extent in a single step, reducing the amount of time and effort required [11].

Table 4: Equilibrium isotherm constants of ACC as for phenol as adsorbent.

Equilibrium Constants	**Values**
Temkin Isotherm	
A (l/g)	0.001
b_1(Jmol^{-1})	0.82
R^2	0.99

Table 5: Kinetic constants of ACC as adsorbents for phenol.

Adsorbent	**Kinetic constants**					
	First-order kinetics			**Second-order kinetics**		
	q_e	k_1	R^2	q_e	h	R^2
ACC	68.93	0.015	0.93	90.91	2.50	0.98

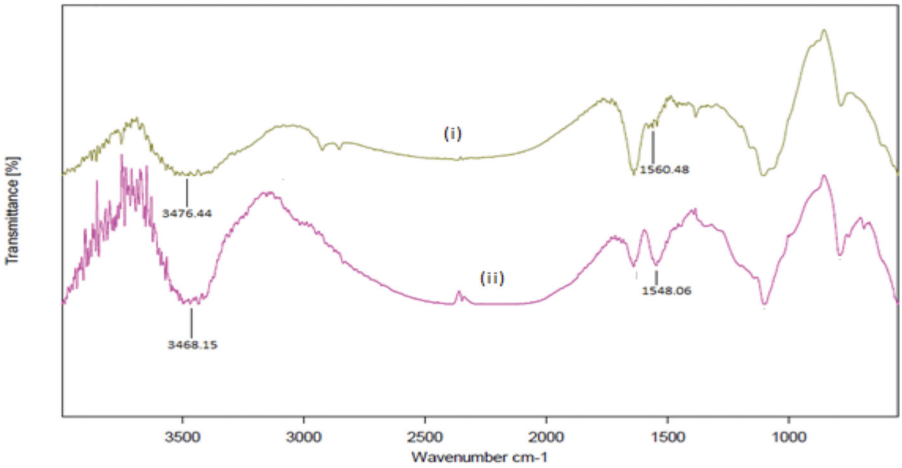


Figure 8: FTIR Analysis on ACC. (i) Before adsorption. (ii) After adsorption.

4. CONCLUSIONS

AC, LA and RI were chosen for the phenol adsorption investigation based on their availability. Because the proportion of phenol removed from aqueous solutions was low, the adsorbents were thermo-chemically treated to produce activated forms such as ACC, LAC and RIC. The material was studied further to establish ACC as the best adsorbent. ACC has a porous structure, which is confirmed by its SEM analysis. The adsorption conditions for phenol elimination were optimised at pH 6.5, 200 rpm agitation and 210 minutes contact time. At a concentration of 97 per cent, the maximum amount of phenol could be removed. The initial phenol concentration, on the other hand, may have no bearing on the process. The adsorption isotherm of ACC was fitted into the Temkin model based on the optimum circumstances chosen. The author was able to analyse the kinetics of the process by the time of contact of the adsorbate-adsorbent system. To varying degrees, ACC fit into first- and second-order kinetic theories. The attachment of phenol to the adsorbent via a donor–acceptor complex mechanism was revealed by its FTIR analysis before and after adsorption.

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