COMPARISON OF BIOMASSES AS ADSORBENT MATERIALS FOR PHENOL REMOVAL

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ABSTRACT

India is a producer of a colossal number of biomasses with high quantity. Even after using them for energy generation, large proportions of residues remain unutilised. They could be utilised as an adsorbent-material to get rid of phenol from aqueous streams. Phenol is listed as highly toxic as per available databases. Thermo-chemical treatment methods have been widely reported to improve the characteristics of biomass-based adsorbents. In this work, based on the availability, three biomasses, Acacia Nilotica Branches (AC), Lantana Camera (LA) and Rice-Husk (RI), were given the treatment. The resulting activated forms of adsorbents were named activated Acacia Nilotica Branches (ACC), activated Lantana Camera (LAC) and activated Rice Husk (RIC). The materials obtained had a high content of fixed carbon, iodine number, BET surface area, and methylene blue adsorption. The operating parameters for sorption in terms of dosage, pH, time of contact, initial phenol concentration and agitation speed were optimised. At these conditions, the adsorption isotherms were compared, and they were explained by Langmuir, Freundlich, and Temkin models. LAC and RIC, respectively highest, followed sorption capacity of ACC. Kinetics of the process on adsorbents considered followed pseudo-first-order and pseudo-second-order models.

Keywords: acacia nilotica branches, adsorbent, adsorption isotherms, adsorption kinetics, adsorption parameters, biomass, characterisation, Lantana camera, rice-husk, 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. The process generates greenhouse gases. 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 gives an account of various biomasses applications as adsorbents for the removal of 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), has 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]. Phenol is listed as a high priority chemical in various databases [10].

In this work, AN, LA and RI were selected based on their suitability [11] and availability in the region. The author's work establishes that the maximum removal of phenol was no more than 35% when the biomasses were used as adsorbent without activation. Properties of AN, LA and RI were compared with commercial-grade carbon. It is observed that the biomasses have much lower BET surface areas, lower fixed carbons (FC) and higher volatile matter (VM). Therefore to upgrade its adsorbent properties, they were given thermochemical treatment based on a literature review [3]. The treatment helped to lower VM and ash percentages, thereby increasing the FC percentages. Consequently, BET surface areas and methylene blue adsorption values of the adsorbents increased. Therefore, activated forms of AN, LA, and RI were abbreviated as ACC, LAC, and RIC.

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The adsorption's operating parameters were effects of dosage, pH, time of contact, initial phenol concentration, and agitation speed. They were optimised for the generation of adsorption curves that fit into Langmuir, Freundlich and Temkin isotherms. The kinetics of adsorption was studied, and they were better explained by pseudo-first-order and pseudo-second-order kinetics. Adsorption of phenol on ACC, LAC and RIC could be studied in the supernatant concentration range of 100 to 975 mg/l.

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. The testing determined moisture, VM, FC and ash percentages of biomasses selected [12].

2.2 Preparation of adsorbents

Biomasses AN, LA and RI were separately acquired, washed and ground in powder form, which passes 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. 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 [12].

2.3 Characterisation of adsorbents

The stored powder of adsorbents (ACC, LAC and RIC) were subject to individual determinations of phenol number, pH, iodine number, methylene blue number, BET surface areas and particle size using standard procedures [12].

2.4 Adsorption experiments on activated biomass materials

For adsorption experiments, the activated adsorbents were taken in 100 ml of phenol solution (1 g/l) at 25°C. The parameters chosen to affect adsorption were dosage, pH, contact time, initial phenol concentration and agitation speed. The phenol concentration was measured using a double beam spectrophotometer. The equilibrium was studied by stirring the solution for 24 hours at 200 pm at the temperature of 25°C. Solutions were maintained at pH ranging from 2.0 to 12.0 with the help of 0.1NaOH and 0.1H_2SO_4. The adsorption parameters were optimised, which were used to study the effect of time on the process. The extent of adsorption was measured at a different time until constancy in phenol removal was ascertained [12].

3 RESULTS AND DISCUSSIONS

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

3.1 Preliminary study of biomasses

Bulk densities of biomasses and proximate analysis were determined on AN, LA and RI as explained in Section 2.1. The bulk density of AN 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 value for RI is 110.0 kg/m^3, meaning; it needs briquetting. 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 all the more suitable to be considered adsorbents [13].

Table 1: Preliminary study of biomasses.

Biomass	**FC (%)**	**Ash (%)**	**VM (%)**	**Bulk density (kg/m^3)**
AN	25	2.50	72.50	210.0
LA	23.50	12.30	64.20	250.0
RI	20.00	18.00	62.00	110.0

3.2 Characterisation of adsorbents

As per earlier studies by the author, selected 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. It has low values of ash and VM [14]. As mentioned in the Materials and Methods section, thermochemical treatment was given to all the biomasses. After comparison, ACC was the best adsorbent (Table 2). It has BET surface area comparable to CGC [15].

Table 2: Characterisation of the activated biomasses chosen as adsorbents [12].

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

3.3 Adsorption experiments on activated biomass materials

The parameters affecting adsorption, namely, adsorbent dosage, initial phenol concentration, agitation speed, contact time, and pH of the adsorbate, were optimised. Fig. 1 indicates that for ACC, LAC and RIC, the removal of phenol increased with dosages. The maximum removal of phenol was possible with 1.2 g of ACC, 1 g of LAC and 1.1 g of RIC.

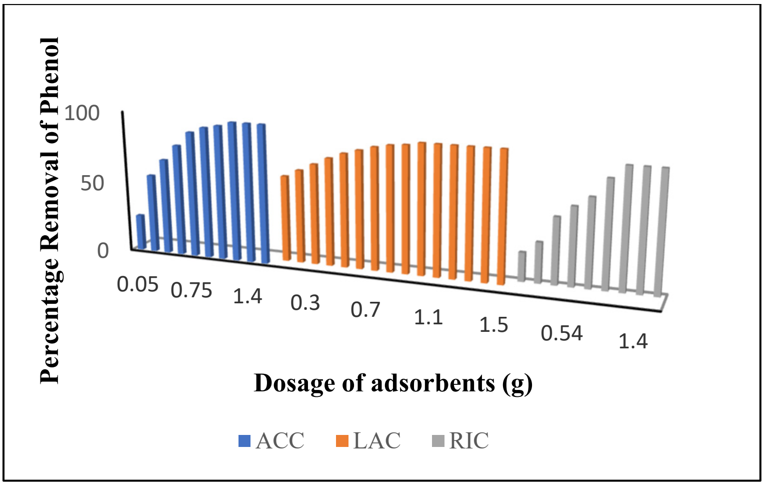

Figure 1: Variation of percentage phenol removal with the dosage of adsorbents.

As pH is one of the parameters for adsorption, its effect was measured. ACC, LAC and RIC best adsorbed the phenol at pH of 6.5, 7.5 and 6.8, respectively. Initial concentrations of phenol in the solution did not affect adsorption [12]. Agitation speed of 200 rpm in the adsorbate-adsorbent system caused maximum removal of phenol at 97%, 90% and 83% by ACC, LAC and RIC, respectively. Speed beyond 200 rpm did not affect the adsorption process.

Time is one of the most critical factors for any adsorption to take place [6]. The parameter was studied at optimised dosage conditions of the adsorbents, pH, initial phenol concentrations, agitation speeds and contact times (Section 2.4). ACC, LAC and RIC removed maximum phenol with a contact time of 4, 5 and 3.5 h correspondingly (Fig. 2).

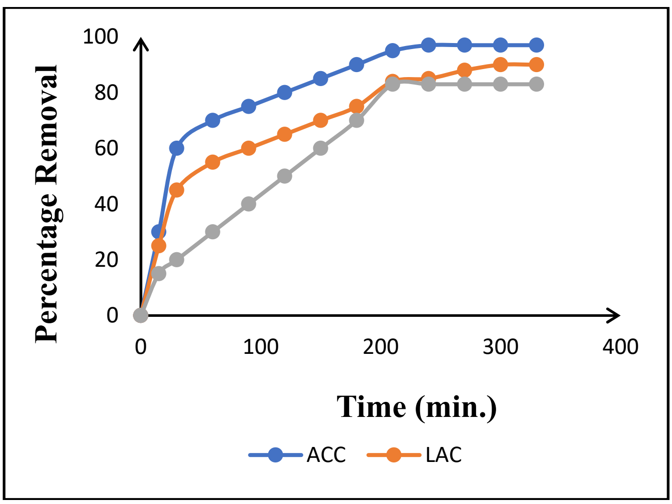

Figure 2: The effect of the contact times on removal of phenol by adsorbents.

3.4 Study of adsorption isotherms of phenol on adsorbents

As per a thorough study of the effects of various parameters on phenol's adsorption on ACC, LAC, and RIC, adsorption isotherms were generated at optimised conditions. For ACC, the isotherm was obtained at a pH of 6.5 and the time of contact of 4 h. For LAC, the equilibrium study was conducted at a pH of 7.5 and the time of contact of 5 h. For RIC, the same was conducted at a pH of 6.8 and the time of contact of 3.5 h. The adsorbate-adsorbent slurries of 100 ml were stirred at 200 rpm at 25°C, for all three cases. The adsorption equilibrium data generated were matched with Langmuir, Freundlich and Temkin isotherms [12], [16]. The results are shown in Table 3.

It was possible to get adsorption isotherm in the concentration range (C_e) of 903 to 975 mg/l for ACC, 100 to 400 mg/l for LAC, 170 to 800 mg/l for RIC. The maximum adsorptions of phenol were 500 mg/g for ACC, 600 mg/g for LAC and 132 mg/g for RIC.

Table 3 confirms that ACC, LAC and RIC follow Temkin, Langmuir and Freundlich isotherms, respectively. There is monolayer adsorption, and the surface is uniform for LAC. Values of k and n for RIC indicate that phenol has strongly attracted towards the adsorbent. The surface of the RIC is heterogeneous [16], [17].

Table 3: Isotherm constants of phenol adsorbed on adsorbents.

Biomasses	**Equilibrium constants**									
	Langmuir				**Freundlich**			**Temkin**		
	Q_0	**b**	**R_L**	**R^2**	**k**	**n**	**R^2**	**A**	**b_1**	**R^2**
ACC	–	–	0.067	–	–	–	–	0.001	0.82	0.99
LAC	16.49	13.95	1.0	0.95	0.31	0.84	0.90	–	–	–
RIC	135.13	0.007	–	0.88	13.52	3.06	0.95	0.05	76	0.90

3.5 Study of adsorption kinetics of phenol on biomasses

The study is significant to know the effectiveness of adsorption. The kinetic data for adsorption were retrieved from Fig. 2. When the values were compared with the first order and second-order kinetics, it was observed that they all fit first-order kinetics closely [17]. The adsorbents ACC and LAC follow second-order kinetics also (Table 4).

Table 4: Kinetic constants of phenol adsorbed on adsorbents.

Biomasses	**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
LAC	85.43	0.012	0.94	103.09	1.84	0.99
RIC	78.72	0.009	0.96	–	–	–

4 CONCLUSIONS

Biomasses, AN, LA and RI selected for the comparison were activated using the thermochemical route resulting in ACC, LAC and RIC as adsorbents. They were compared for their physical, chemical and adsorbent properties. Ash content reduced to 1.0% for ACC, whereas LAC and RIC are 5.0% and 4.80%, respectively. FC for all activated biomasses is high and comparable at 87.0%, 85%, and 84.2%. ACC, LAC and RIC confirmed high BET surface areas comparable to CGC. The maximum removal of phenol by ACC, LAC, and RIC was 97%, 90%, and 83% individually. Factors affecting the adsorption process were optimised. RIC got to fit into first-order-kinetics, whereas ACC and LAC followed second-order kinetics. Thus biomasses AN, LA and RI after activation proved as promising adsorbent materials for removal of phenol. They have opened the possibility for their utilisation as adsorbents to remove other organic pollutants from the industrial effluents.

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