Removal of Acetaminophen from Waste Water using Low Cost Adsorbent

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Abstract: - The present work aims to investigate the removal of acetaminophen which is also known as paracetamol by using activated carbon which is developed from agricultural waste namely banana leaves, garlic stem, babool seeds. The effect of various parameters has been studied such kinetic results, adsorption, removal efficiency, equilibrium amounts and time. The maximum removal efficiency obtained was 84.9% for banana leaves absorbent with 10 mg activated carbon dose having sample of 25 ml at 30°C.

The analysis was done for sample 25 ml, 50 ml, and 100 ml for BL, GS, and BS. This has shown that activated banana leaves has achieved removal amount equivalent to that of common activated carbon. Therefore, activated banana leaves have potential to be a good adsorbent.

Keywords- Pharmaceuticals, removal efficiency, banana leaves, garlic stem, babool seed.

1. INTRODUCTION

Adsorption is a well-established technique to remove pollutants, being activated carbon (AC) the preferred adsorbent for remediation of water with low pollutant concentration. Activated carbons are known to be very effective adsorbents due to their unique combination of a highly developed porous network coupled with its ability to react with other heteroatom creating a variety of surface functionalities on its surface and within the structural framework **[1,2]**. Due to their versatility, ACs have been studied not only as adsorbents, but also as catalysts and catalyst supports, in many different purposes such as the removal of pollutants from gaseous or liquid phases and for the purification or recovery of chemicals **[1,2]**. Despite such features, the implementation of activated carbons on large scale industrial processes is limited due to a poor economic feasibility associated with its manufacture and regeneration costs **[3]**. Consequently, activated carbons are often replaced by costly effective adsorbents (sepiolites, diatomites) in many industrial applications, even if their removal efficiency is much lower from that of AC.

The economic cornerstone for the use of activated carbons in advanced water treatments based on adsorption processes can be overcome by exploring new synthetic routes to lower the production costs of activated carbons, or using non expensive materials (such as non-valuable by-products or residues) as precursors for their preparation. In this sense, the utilization of residues as precursors of carbon adsorbents is an interesting strategy that enables to deal with the problem of waste disposal and recycling **[4–11]**. On the other hand, it is well known that that the chemical and textural properties of activated carbons does not depend only on the activation conditions (temperature of carbonization and activation, heating rate, nature and ratio of activating agent, etc.), but also on the chemical composition of the raw precursor (its intrinsic reactivity), as well as on how those carbons are handled (aging effect) afterwards **[2].** Thus, the use of residues for the preparation of AC seems very attractive from the point of view of obtaining low cost adsorbents, but still the choice of the precursor may define their final applicability.

In this work we have explored the synthesis of adsorbents from residues of different nature, comparing the physical and chemical features of the prepared materials upon the nature of the precursor, and assessing the potential application of these adsorbents in water remediation for the removal of an analgesic. We have used several widely produced residues for the preparation of carbon materials: Banana Leaves, Garlic Stem and Babool seed.

This study is carried out on characterization and treatment of wastewater discharged from a pharmaceutical unit. The wastewater samples were collected on a wastewater laboratory scale operations and analyzed both in raw and treated form. To increase the knowledge of people towards this disastrous pollution this research is been started.

The objective of this study was to link the characteristics of the prepared adsorbents with the removal efficiency of the target compound. Our interest was to identify the best adsorbent, not only on the basis of the cost of the activated carbon but also on its adsorption capacity. As probe molecule, we have selected acetaminophen which is also known as paracetamol, and is one of the most worldwide consumed analgesics.

2. METHODS

2.1 Adsorbent preparation

Several activated carbons have been prepared from agricultural residues, namely Banana Leaves (BL), Garlic Stem (GS) and Babool seed (BS) for the adsorption of acetaminophen from aqueous phase. These residues were cleaned using tap water to eradicate possible strange materials present in it (dirt and sands). Washed sample material was air dried for 2-5 days before use and then crushed in order to reduce the size. The crushed materials were found to be 75 g in weight. The precursors were immersed in H_2SO_4 solution (1% by weight/volume) in ratio 1:2 of precursors. The mixture was put in a crucible and placed in a Hot air oven for carbonization. The heating temperature for carbonization was maintained at 150 °C for 24 hours. The produced activated bamboo was then cooled down to room temperature. To remove impurities like ash activated bamboo was washed with 0.1 N aqueous solution of NaOH followed by washing with distilled water several times until the PH of the washing solution was neutral and then it was dried in hot air oven at the temperature of 60 °C for the period of 24 hours.

2.2 Adsorption from solution

Acetaminophen, also known as paracetamol, (N-(4- hydroxyphenyl)ethanamide, $C_8H_9NO_2$). All the solutions were prepared with ultra-pure. The solutions were used as prepared, that is, without pH adjustment, presenting values around 5.8 units.

Equilibrium adsorption studies were made at 30 ◦C, 15 ml of acetaminophen (ACE) solution (initial concentration 120mg/l) were mixed with 10mg of activated carbon in glass vials and continuously stirred (700 rpm) at a controlled temperature of 30 °C in a water bath. The time recording was started when the stirring began and several samples were collected between 30 min and 24 h. All adsorption assays were made in triplicate. After filtration, the residual concentration (C) of acetaminophen remaining on the solution was analyzed in a UV–vis spectrophotometer (Shimadzu UV-2000) at 540nm. The amount adsorbed was determined according to

$$q = \frac{Co-C}{W}.V \qquad \text{.....} \quad \textbf{(1)}$$

Where q is the amount (mg/g) adsorbed at time t, Co is the initial concentration (mg/l), C is the concentration at time t (mg/l), and V is the volume (l) of the adsorbate solution and W is the weight (g) of dried carbon.

The Study of the adsorption from solution at 30 ◦C done by varying acetaminophen solution concentration (30–180 mg/l), solution volumes (25, 50 and 100) and keeping adsorbent dose at 10 mg. The acetaminophen remaining in solution (C_e) was assessed as described above and the uptake (q_e) was calculated using Eq. (1).

Table 1: Concentration and amount adsorbed of acetaminophen from 15 ml sample with 10mg Activated Carbon dose and 120 mg/l initial concentration of ACE

Time (min)	C/Co			q(mg/g)		
	BL	GS	BS	BL	GS	BS
0	1	1	1	0	0	0
30	0.64	0.84	0.93	64.8	28.8	12.6
60	0.43	0.69	0.83	102.6	55.8	30.6
90	0.32	0.55	0.77	122.4	81	41.4
120	0.21	0.43	0.664	142.2	102.6	60.48
150	0.19	0.39	0.56	145.8	109.8	79.2
200	0.189	0.37	0.45	145.98	113.4	99
300	0.179	0.374	0.43	147.78	112.68	102.6
400	0.176	0.371	0.428	148.32	113.22	102.96
500	0.162	0.368	0.421	150.84	113.76	104.22
600	0.162	0.362	0.42	150.84	114.84	104.4
700	0.164	0.363	0.42	150.48	114.66	104.4
800	0.164	0.364	0.415	150.48	114.48	105.3
900	0.163	0.363	0.41	150.66	114.66	106.2

Fig 1(a) Kinetic results of acetaminophen adsorption at 30 ◦C ([ACE] = 120 mg/l), activated carbon dose 10 mg/15 ml of solution).

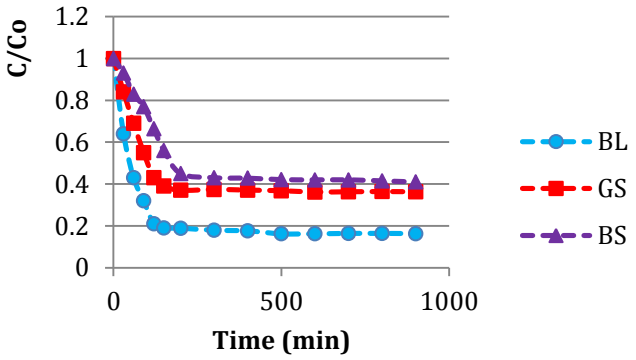
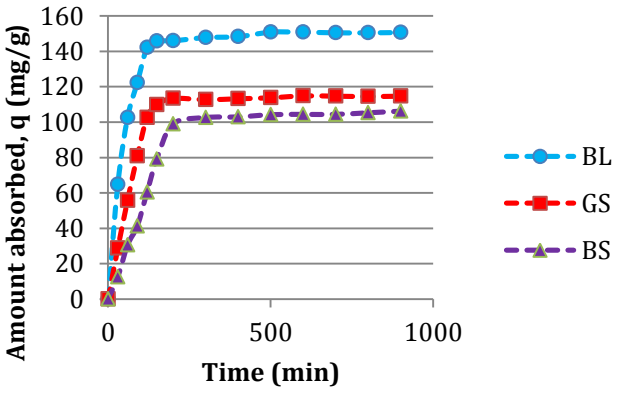


Fig 1(b) Amount adsorbed of ACE by various adsorbents at 30 ◦C ([ACE] = 120 mg/l), activated carbon dose 10 mg/15 ml of solution).



3. RESULTS AND DISCUSSION

The aim of this work was to investigate the feasibility of an adsorption process using activated carbons for the removal of a common analgesic frequently found in wastewater and treated water from urban sewage facilities. For this reason, we have selected three activated carbons – prepared from different precursors and therefore exhibiting varied porous features and chemical composition – and a series of activated carbons in-house prepared from various residues. Details of the preparation of the activated carbons, as well as the optimization of various synthesis conditions and their effect on the properties of prepared materials have been deeply discussed in previous studies so would remain out of the scope of this paper. Nevertheless, their characteristics are herein showed for data interpretation purposes.

3.1 Point of Equilibrium

Fig. 1(a)(b) shows the evolution of acetaminophen (ACE) concentration with time for the studied activated carbons, and the results show large differences in the performance of the adsorbents. Adsorption almost attains equilibrium after 10 hr and the experimental adsorption isotherms for ACE on the studied carbons are illustrated in Fig. 3(a)(b)(c). Equilibrium was reached within 10 h for all the carbons, with the exception of carbon BS where slight change in concentration observed after 10 hr. BL displays the fastest ACE uptake with average 83.8% removal of ACE. The values obtained for the adsorbents prepared from Agricultural residues follow the trend: BL>GS>BS.

The shape of the ACE adsorption kinetics indicates hyperbolic relations with time imply adsorption kinetic is of second order. The adsorption isotherms display a concavity towards the abscissa axis in all cases, indicating that as more sites in

the substrate are filled, it becomes more difficult for a fresh solute molecule to find a vacant site. This implies that there is no strong competition of the solvent for the adsorption sites. At high equilibrium concentration of ACE in solution, the amount adsorbed steadily increased and the adsorption isotherms display a plateau indicating the formation of a complete monolayer.

3.2 Removal efficiency (RE)

The removal efficiency (RE) was calculated after 10 h according to the equation 2:

$$RE=[(Co-Ce)/Co]\times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \textbf{(2)}$$

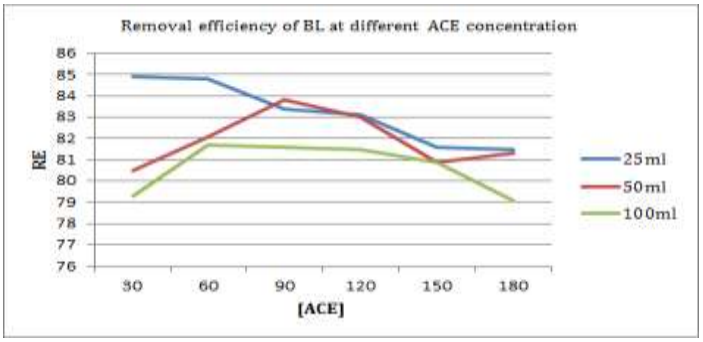
Where Co and Ce are the initial and equilibrium acetaminophen concentrations, respectively; values are plotted below. The values obtained follow the trend: BL>GS>BS. The largest value is attained for BL 83.8% and after that 63.8%, 58% for GS and BS respectively. Large differences are also observed in the rate of adsorption of the studied carbons at short times (early adsorption stage). It is interesting to remark here that from a chemical point of view, the residue-derived carbons seem to be adequate for the uptake of acetaminophen due to their intrinsic basicity, which is linked to the nature of the carbon precursor.

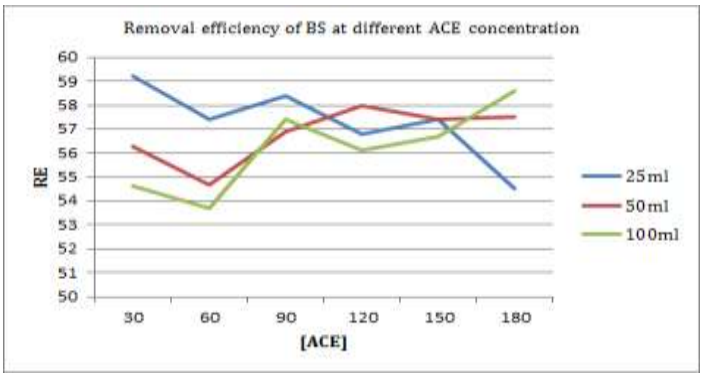
Moreover, any competitive effect due to adsorption of water molecules on the adsorbents can be disregarded, in the view of the hydrophobic character of the studied activated carbons. Hence the differences in ACE uptake and rate of adsorption have to be explained in terms of the variability of the textural properties of these activated carbons, which is somehow linked to the preparation method and precursor's nature.

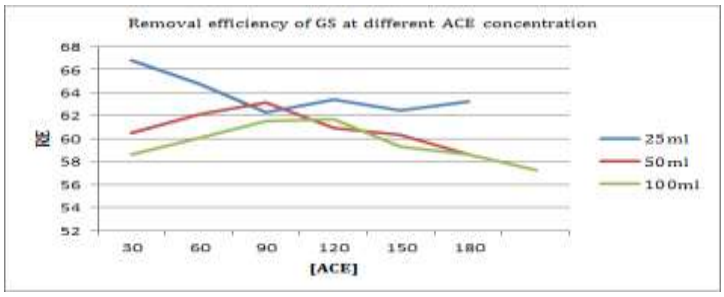
As abovementioned, considering the basic nature of all the adsorbents, a similar adsorption mechanism is expected for ACE retention, being dispersive forces the dominant interactions. However, the oxygen content also affects the hydrophobic/hydrophilic nature of the adsorbents. In fact, the carbons synthesized from lignocellulosic precursors have large amounts of oxygen that render them an important hydrophilic character. Thus, it seems reasonable to expect that the wettability of these carbons is favored in aqueous solutions.

Table 2 Equilibrium Concentration of ACE, amount adsorbed of ACE and removal efficiency of AC's from different sample with 10mg Activated Carbon dose and different initial concentration of ACE

Sample	C	C_e			q_e			RE (%)		
		BL	GS	BS	BL	GS	BS	BL	GS	BS
25ml	30	4.54	9.97	12.23	63.65	50.075	44.425	84.9	66.8	59.2
	60	9.12	21.14	25.54	127.2	97.15	86.15	84.8	64.8	57.4
	90	14.96	33.91	37.4	187.6	140.23	131.5	83.4	62.3	58.4
	120	20.23	43.88	51.89	249.43	190.3	170.28	83.1	63.4	56.8
	150	27.54	56.3	63.86	306.15	234.25	215.35	81.6	62.5	57.4
	180	33.34	66.16	81.88	366.65	284.6	245.3	81.5	63.2	54.5
50ml	30	5.86	11.86	13.11	60.35	45.35	42.225	80.5	60.5	56.3
	60	10.72	22.72	27.2	123.2	93.2	82	82.1	62.1	54.7
	90	14.59	33.18	38.8	188.53	142.05	128	83.8	63.1	56.9
	120	20.44	46.89	50.4	248.9	182.78	174	83	60.9	58
	150	28.59	59.48	63.9	303.53	226.3	215.25	80.9	60.3	57.4
	180	33.64	74.61	76.5	365.9	263.48	258.75	81.3	58.6	57.5
100ml	30	6.21	11.97	13.62	59.475	45.075	40.95	79.3	60.1	54.6
	60	10.98	23.11	27.8	122.55	92.225	80.5	81.7	61.5	53.7
	90	16.59	34.5	38.3	183.53	138.75	129.25	81.6	61.7	57.4
	120	22.24	48.85	52.74	244.4	177.88	168.15	81.5	59.3	56.1
	150	28.59	62.12	64.9	303.53	219.7	212.75	80.9	58.6	56.7
	180	37.63	76.83	74.56	355.93	257.93	263.6	79.1	57.3	58.6







3.3 Equilibrium Amount adsorbed

The amount adsorbed was determined according to

$q_e=[(Co-C)/W]*V$ …… **(3)**

Fig 3(a). Equilibrium adsorption isotherms v/s Equilibrium remaining concentration of acetaminophen on the investigated carbons at 30 ◦C, activated carbon dose 10 mg, 25ml sample

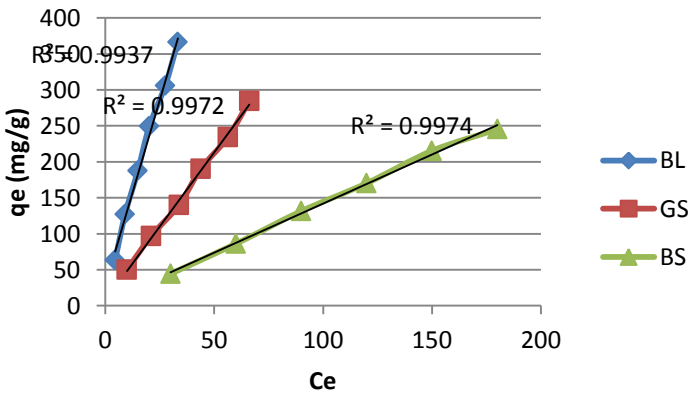


Fig 3(b). Equilibrium adsorption isotherms v/s Equilibrium remaining concentration of acetaminophen on the investigated carbons at 30 ◦C, activated carbon dose 10 mg, 50ml sample

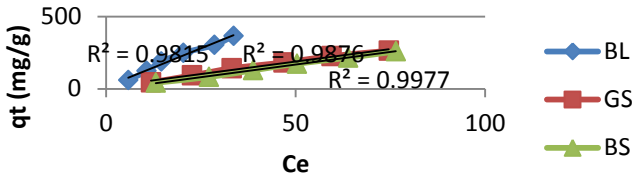
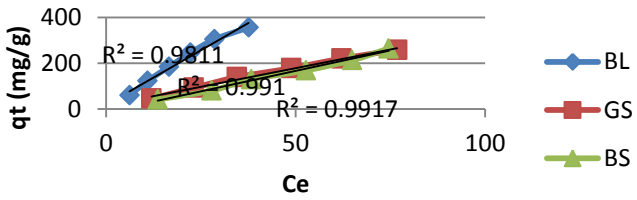


Fig 3(c). Equilibrium adsorption isotherms v/s Equilibrium remaining concentration of acetaminophen on the investigated carbons at 30 ◦C, activated carbon dose 10 mg, 100ml sample



4. CONCLUSIONS

The potentialities of activated carbons obtained from various wastes for the removal of acetaminophen were investigated. The characterization of the materials revealed that the adsorption of ACE is a complex process that depends strongly on the characteristics of the adsorbent. Following remarks can be made from above study according to our objectives;

- Removal efficiency: The values obtained follow the trend: BL>GS>BS. The largest value is attained for BL 83.8% and after that 63.8%, 58% for GS and BS respectively.
- It has been concluded that for a sample of 25 ml BL was found to give highest removal efficiency of 84.9% then after GS and BS.
- Adsorption of 15 ml sample with 10g adsorbent and [ACE]=120mg/l almost ceases after 600 min (i.e. time require to achieve equilibrium is 10 hr for all adsorbent) at 30^0C.
- Fitting data to the Freundlich Equation gives value of n nearly equal to 1 for all adsorbent while value of k is greater for BL, shows BL shows faster uptake at low concentration of ACE.
- At low equilibrium concentration of ACE n=1 gives Freundlich Equation (qe=kCe) means qe v/s Ce also straight line.

To conclude, as all activated carbon were obtained from agricultural residues. This is found to be cost effective in nature. The result of removal proves to be almost equivalent to that of expensive activated carbon.

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