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Adsorption of polluting substances on activated carbons prepared from rice husk and sugarcane bagasse

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Abstract

Rice husk and sugarcane bagasse were chemically impregnated with $ZnCl_2$ and carbonized at 700 °C in a large-scale rotary furnace. The activated carbons (ACs) obtained had BET surface area of 811 and 864 m^2/g, respectively, and were essentially microporous. The adsorption of arsenic, humic acid, phenol and a municipal solid waste landfill leachate was examined. Both ACs showed the best adsorption behaviour towards phenol, removing around 80% at the equilibrium time of 4 h. The adsorption isotherms for arsenic and humic acid were also favourable, although the maximum loadings achieved were lower than that of phenol. Finally, the rice husk AC showed 60% and 70% removal efficiency for colour and COD, respectively, when tested on a landfill leachate.

Keywords: Rice husk; Activated carbon; Sugarcane bagasse; Landfill leachate; Arsenic; Humic acid; Phenol; Adsorption

1. Introduction

Activated carbon (AC) products are produced from organic materials that are rich in carbon. The choice of precursor is largely dependent on its availability, cost and purity. The precursor and the method used for activation largely determine the adsorption properties of the AC. Typical precursors for activated carbon production are coal, lignite, wood, nut shells, peat, coke, etc. ACs can be prepared by either physical or chemical activation. Physical activation is usually a two-stage process (pyrolysis–activation) that employs gases such as nitrogen, steam, carbon dioxide, air or mixtures of the above, without the presence of a catalyst. Activation occurs at temperatures above 700 °C at residence times that vary between 30 min and several hours. Chemical activation involves a pre-treatment scheme (impregnating step) where the material is mixed with a chemical before the activation process. The most widely used chemicals include H_3PO_4, H_2SO_4, KOH, NaOH and $ZnCl_2$. Impregnation can take up to 24 h depending on the chemical used, the precursor and the subsequent activation process. ACs with high surface area can be obtained at lower temperatures, compared to the temperatures required for physical activation. In a comprehensive review regarding the use of agricultural residues as precursors for AC production, Ioannidou and Zabaniotou [1] provide critical information with respect to the type of residue, process parameters, activation type and desirable use of the AC. Biowaste originated activated carbons with BET surface areas ranging from 250 to 2410 m^2/g and pore volumes ranging from 0.022 to 91.4 cm^3/g have been reviewed and compared.

Many researchers have investigated the use of agricultural by-products as precursors for the production of ACs with high adsorptive capacity. Date and olive stones, coconut and almond shells, rice husks (RH) and sugarcane bagasse (SB) are only few of the materials that have been successfully used for the preparation of ACs [2–9]. Ng et al. [10], produced activated carbon from pecan shells by double-stage steam activation at 850 °C for 2 h after carbonization at 700 °C for 1 h. Surface areas resulted were in the range of 750–850 m^2/g. Physical activation of dry bagasse in a two-stage carbonization/activation process within a temperature range of 750–840 °C produced activated carbon with significant surface areas (404–607 m^2/g), the surface area increasing with increasing temperature [11]. In a recent study, Zabaniotou et al. [12] investigated the production of ACs from olive kernels in two different modes: laboratory-scale pyrolysis

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followed by chemical activation with KOH and (b) pilot/bench-scale pyrolysis followed by physical activation with H_2O–CO_2. The maximum BET surfaces obtained were 1000–1200 m^2/g and 3049 m^2/g at industrial scale with physical activation and at laboratory scale with chemical activation, respectively.

Apart from the two-stage physical activation process, a number of researchers have investigated a single-stage physical activation process, when carbonization/activation takes place simultaneously. Savova et al. [13] applied a one-step pyrolysis process to almond shells, nut shells, peach stones, cherry stones and grape seeds. The process involved direct heating of the precursors with steam at a rate of 15 °C/min and 1 h retention time at 800 °C. The best results were obtained for apricot stones with a surface area of 1190 m^2/g, followed by almond shells at 998 m^2/g, cherry stones at 875 m^2/g, nut shells at 743 m^2/g and grape seeds at 497 m^2/g.

Girgis et al. [14], compared three activating agents, KOH, H_3PO_4 and $ZnCl_2$ for the activation of rice hulls. Of the three, H_3PO_4 produced carbons with the highest surface area of 1177 m^2/g. KOH after pyrolysis and 3 h heating at 500 °C resulted in activated carbon with 268 m^2/g surface area and $ZnCl_2$ after 6 h pyrolysis at 300 °C and 3 h heating at 750 °C resulted in 420 m^2/g surface area. All chemicals performed better than steam activation alone. Caturla et al. [15] impregnated peach stones with concentrated $ZnCl_2$ at ratios ($ZnCl_2$:material) 0.4:1–2.5:1. The impregnated mixture was kept at 85 °C from 7 to 24 h under evaporation, partial evaporation and no evaporation conditions. The material was then heated under N_2 at 500–800 °C. The produced carbons had surface areas up to 3000 m^2/g. Increasing the $ZnCl_2$:material ratio from 0.2:1 to 1:1 increased the surface area from 1000 to 2000 m^2/g. Further increase of the ratio resulted in a decrease of the surface area. An increase of temperature from 600 to over 1000 °C leads to a decrease of surface area. Through chemical activation with KOH, Stavropoulos and Zabaniotou [16] produced ACs with high surface area (>1300 m^2/g) from olive seed waste residues. The highest surface area (3049 m^2/g) was achieved when activation occurred at 900 °C and 4 h residence time. Their carbons also showed high adsorptive capacity with respect to methylene blue.

Due to their adsorption properties, ACs are used for the removal of a wide range of pollutants from wastewaters, such as heavy metals, phenols, dyes and other polar and non-polar organic substances [17–19]. Activated carbons produced from almond shells, pecan shells and walnut shells either by chemical or physical activation removed almost 100% of lead ion, 90–95% of copper ion and 80–85% of zinc ions when used in a "point of use" drinking water filter system [20]. Regarding VOCs' adsorption, activated carbons prepared from almond and pecan shells by chemical, CO_2 and steam activation were compared to commercial products made from coal and coconut shells [21]. Commercial products adsorbed 480–520 ppb of VOCs per gram of carbon, with the coconut shell product being superior. The adsorption capacity of the produced carbons ranged from 350 to 510 ppb VOCs/g of carbon. Although the chemically activated carbons had a larger surface area, their adsorption capacity was inferior to that of the physically activated carbons. Toles et al. [22] produced a series of activated carbons from almond shells with surface areas from 200 to 600 m^2/g and compared them to commercial activated carbons of 950 m^2/g surface area for the removal of polar and non-polar organic compounds. Results showed that nearly all carbons (except the one with BET 200 m^2/g) performed, on average, equally well compared to the commercial ones. Recently, Skodras et al. [23] reviewed the adsorption of mercury in ACs prepared from biomass materials and waste tires. They prepared ACs from pine/oak woods through physical activation and from olive seeds through chemical activation with KOH. One of the main conclusions was that an increase in the surface area of the ACs results in an almost proportional increase in the Hg adsorption capacity. The olive seed ACs showed better adsorption properties compared to the pine wood or oak wood ACs.

Kula et al. [24] studied the adsorption of Cd(II) on ACs prepared from olive stones by $ZnCl_2$ activation. The adsorption experiments they performed indicated that the activated carbon from olive stone has a good adsorption capacity for Cd(II) ions from aqueous solutions. Specifically, at a Cd(II) concentration of 45mg/L, the highest adsorption capacity was 1.654 mg/g.

In addition, ACs were demonstrated to have excellent effectiveness in the removal of organic matter and nitrogenous substances in landfill leachates. Rivas et al. [25,26] studied some integrated processes treating landfill leachates. The systems tested included adsorption onto activated carbon. COD removals obtained ranged from 80% to 96% for initial COD values close to 11000 mg/L, although none of the processes tested reduced the COD levels sufficiently to allow direct discharge.

Recently, Kurniawan et al. [27] reviewed the main physico-chemical treatments for landfill leachate. According to the authors, none of the individual physico-chemical techniques is universally applicable or highly effective for the removal of recalcitrant compounds from stabilized leachate. A combination of physico-chemical and biological treatments has demonstrated its effectiveness for the treatment of stabilized leachate. Biological treatment alone usually results in low COD removals, because of high COD, high ammonium-N content and presence of toxic compounds. A pre-treated leachate was subjected to adsorbent-supplemented biological treatment in an aeration tank operated in fed-batch mode [28]. COD and NH_4^+-N removal performances of powdered activated carbon (PAC) and powdered zeolite were compared during biological treatment. Percent COD removals with PAC addition were significantly higher than those obtained with the zeolite. However, zeolite performed better than the PAC in ammonium-N removal from the leachate.

Addition of landfill leachate to a domestic wastewater treatment system may have negative impact, since leachate is a highly concentrated wastewater both in terms of inorganic and organic pollutants. A recent research revealed that the negative impact of leachate on a municipal wastewater treatment system could be prevented by the addition of PAC [29].

In all the above studies, the ACs employed for the adsorption tests had significant surface areas and adsorption capabilities, in many cases comparable to the commercially available carbons. However, their production methods involved several stages of preparation, long retention times for pyrolysis and activation and often elevated temperatures. The present study aimed at testing the adsorption properties of ACs that were prepared in a single activation process in relatively short retention times. Model pollutants such as phenol, humic acid and arsenic were used. Additionally, the adsorption of highly contaminated leachates generated in a municipal landfill onto three different adsorbents: two activated carbons (the rice husk AC produced in this work and one commercial AC) were investigated, both in terms of contaminant level reduction per unit mass of absorbent and in terms of the process kinetics.

2. Materials and methods

2.1. Precursor materials

Sugarcane bagasse was obtained from Ajnala Cooperative Sugar Mill on the district of Amritsar in India in the form of a sheaf of bagasse. Bagasse was dried in an oven at 110 °C for 6 h. It was then ground with a microhammer cutter mill and sieved to a 10 or 32 mesh (2.0 mm or 500 μm) particle size prior to activation. Bagasse with a particle size of 500 μm was used for characterization and the production of activated carbons.

Rice husk was obtained from Janta Rice Mill in Gurdaspur in India. Rice husk was initially washed thoroughly with water to remove any impurities, dried at 110 °C for 6 h and then ground with a microhammer cutter mill and sieved to a 10 or 32 mesh (2.0 mm or 500 μm) particle size. The finer fraction was used for characterization and for the activation studies. The properties of the raw materials are shown in Table 1.

2.2. Activation method and apparatus

Table 1
Properties of rice husk and sugarcane bagasse

	Rice husk	Sugarcane bagasse
Moisture (%)	4.2	6.1
Ash content (%)	16.1	3.3
Volatile matter (%)	62.0	65.9
Fixed carbon (%)	17.7	24.7

The choice of the optimum experimental parameters for the impregnation and activation of rice husk and sugarcane bagasse were based on preliminary laboratory-scale experiments performed under the 6th FP EU–India Economic Cross Cultural Programme Project titled 'Production of High Added Value Products for Environmental Applications from Agricultural By-products in India: Activated Carbon Production from Bagasse and Rice Husks' [30]. In these experiments, dried and ground (≤0.5 mm) rice husk and bagasse were impregnated with $ZnCl_2$ at ratios of 0.25 to 1. Distilled water was added at a quantity amounting to 10 times the total weight of the solid mixture. The mixture was then stirred and heated to make homogeneous and impregnated at a temperature of 80–100 °C. A thick uniform paste was obtained after 2 h. A sample of wet paste (around 75% moisture) was weighed before being fed to the reactor for a single step of carbonization/activation.

The optimum $ZnCl_2$-to-rice husk ratio was 1:1 and for bagasse this ratio was 0.75:1.The optimum experimental conditions were found to be 700 °C carbonization/activation temperature and 30 min residence time. At these conditions, the AC surface areas obtained were 674 and 750 m^2/g for rice husk and bagasse, respectively. For this study, the optimum impregnating ratios were followed and the optimum temperature and residence time were applied to obtain ACs from a large-scale reactor.

Fig. 1 shows the main components of the AC production unit and their dimensions (in cm). The experimental set up of the reactor consisted of a mechanical screw feeder connected to a cylindrical rotary furnace chamber, and an AC collection box. A gas inlet line was fitted at the end of the screw feeder and two gas outlet lines were fitted on top of the collection box to avoid accumulation of gaseous by-products in the furnace.

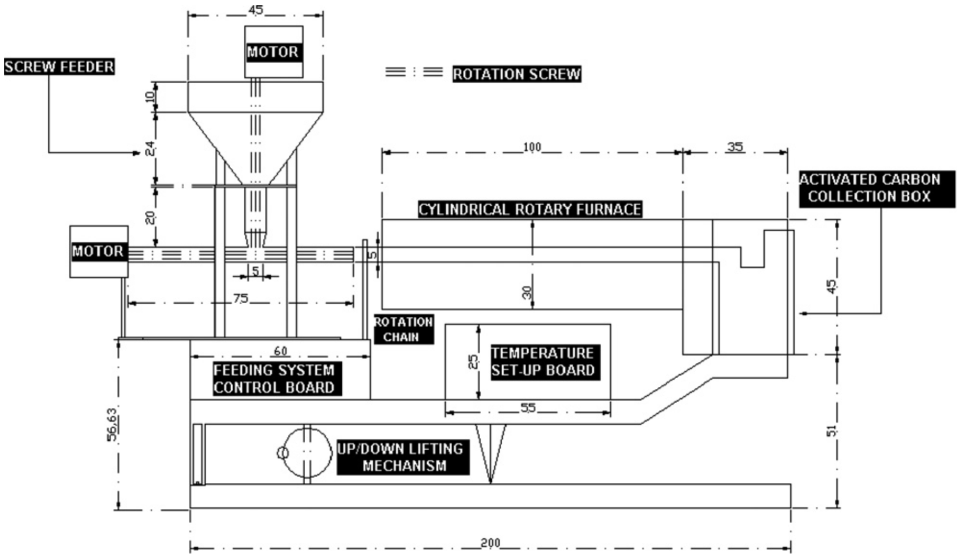

Fig. 1. Diagram of the main components of the AC production unit.

The rotation rate of the screw feeder (i.e. the speed at which the paste entered the furnace) was controlled through a control board. The required residence times were achieved by adjusting the inclination of the furnace (through a mechanical lever shown in Fig. 1) in conjunction with the speed of furnace rotation.

Nitrogen gas was allowed to pass through the reactor (4 L/min) in order to remove air from the system. The furnace was heated to 700 °C, and once the target temperature was reached (approximately 30 min), the gas supply was changed from nitrogen to CO_2 (5 L/min) and the feeding of the paste commenced. The residence time required for activation was 30 min. The ACs were obtained in the collection box in crude form (lumps of 0.2–1.5 cm) and were allowed to cool to room temperature. Then they were mechanically crushed and thoroughly washed with a solution of HCl 0.1 M to remove excess Zn and other impurities. Finally, the ACs were washed with distilled water and dried at 105 °C for 6 h.

2.3. Characterization of the activated carbons

Each activated carbon's surface area was determined from nitrogen adsorption data obtained with a gas sorption analyzer (NOVA 2200, Quantachrome). The samples were degassed under vacuum at 300 °C for 8 h prior to measurement. The adsorption equilibrium time was set at 90 s. The Brunauer–Emmett–Teller (BET) method was used to calculate the surface area, based on selected N_2 adsorption data within the p/p_o range of 0.025–0.3 [31].

The total pore volume (V_{total}) and the average pore diameter (d_{av}) were derived from the Barrett, Joyner and Halenda (BJH) method [32]. The micropore volume (V_o) was calculated according to the Dubinin–Radushkevich (DR) method [33,34]. The particle size distributions were measured in a particle size analyzer (Mastersizer S, Malvern) equipped with an optical measurement unit and a sample suspension unit. The lens used was type 300 RF, able to detect particle sizes in the range of 0.05–880 μm.

The ash content of the carbons was determined using the standard ASTM procedure D2866-94. This method involves heating the sample at 650 °C for several hours until constant weight has been achieved. The ash is then weighed and the ash content of the activated carbon is calculated as follows:

$$\text{Total ash}\ (\%) = \left[\frac{(D-B)}{(C-B)}\right] \times 100 \tag{1}$$

where B is the weight of the crucible (g), C is the weight of the crucible plus original sample (g) and D is the weight of the crucible plus ash containing sample (g).

The pH of the carbons was determined using the standard test of ASTM D 3838-80. This procedure involves heating 10 g of carbon in 100 mL of distilled water to its boiling point for 15 min. The slurry is then filtered and the pH of the filtrate is measured at 50 °C.

The adsorption capacities of the carbons were then tested using solutions of phenol, arsenic, and humic acid, as well as leachate from a municipal solid waste (MSW) landfill.

2.4. Adsorption of phenol

For the adsorption of phenol, a 10 ppm stock solution of phenol was prepared. Seven Erlenmeyer flasks were used, each one of them containing 0.03, 0.05, 0.08, 0.1, 0.13, 0.15, and 0.18 g of AC and 200 mL of the stock solution, respectively. The adsorption of phenol was initially tested on both rice husk AC and sugarcane bagasse AC. The flasks were mechanically shaken for 9 days and the solutions were then filtered through a 0.45 μm polypropylene membrane filter to separate the liquid from the AC. The percentage of phenol removal was determined by measuring the phenol remaining in solution using a UV spectrophotometer at a wavelength of 269 nm. The adsorption data were analyzed in terms of the Langmuir and Freundlich model isotherms using the equations:

$$q = \frac{QbC_e}{1+bC_e} \tag{2}$$

and

$$q = KC_e^{1/n} \tag{3}$$

respectively, where q is the mass of adsorbate per mass of adsorbent, C_e is the equilibrium concentration of adsorbate in solution and Q, b, K, n are constants for a given adsorbate and adsorbent at a particular temperature.

To study the kinetics of phenol adsorption, a 100 ppm stock solution of phenol was prepared. Six Erlenmeyer flasks were used, each containing 100 mL of the stock solution and 0.2 g of rice husk AC. The flasks were mechanically shaken and progressively removed at appropriate time intervals.

2.5. Adsorption of arsenic

To test the adsorption capacities of the rice husk and sugarcane bagasse ACs, a 10 ppm stock solution of As was prepared in the form of AsO_4^{3-}. Nine separate Erlenmeyer flasks were used, each one of them containing 0.2, 0.4, 0.6, 0.8, 1.1, 1.4, 1.8, 2, and 2.2 g of rice husk AC, respectively, and 200 mL of the stock solution of As. The flasks were then mechanically shaken for 96 h at 180 rpm to achieve equilibrium between As and the carbon surface [35]. At the end of the process, the solutions were filtered through a 0.45 μm polypropylene membrane filter to remove the AC and the filtrates were prepared for analysis according to the molybdate blue method [36]. The percentage of As removal was determined by measuring the As remaining in solution using a UV spectrophotometer at a wavelength of 885 nm.

2.6. Adsorption of humic acid

For the adsorption of humic acid, a 20 ppm stock solution of humic acid was prepared. Eight Erlenmeyer flasks were used, each one of them containing 0.1, 0.2, 0.3, 0.4, 0.7, 0.9, 1.2, and 1.4 g of AC, respectively, and 200 mL of the stock solution. As in arsenic adsorption case, only the rice husk AC was used. The flasks were mechanically shaken for 7 days at 180 rpm and the solutions were then filtered through a 0.45 μm polypropylene membrane filter to separate the liquid from the AC [35]. The percentage of humic acid removal was determined by measuring the humic acid remaining in solution using a UV spectrophotometer at a wavelength of 254 nm.

2.7. *Activated carbon treatment of a landfill leachate*

The landfill leachate used in this work was collected from the storing unit of the liquid waste generated by the municipal solid waste organic fraction (before composting), in an integrated MSW plant located in Seville (Spain). Given the high content of contaminants in the raw leachate sample, it was diluted up to 10% using tap water for all the laboratory adsorption tests. After that, the diluted leachate sample was filtered through a GF/C glass fibre filter.

The diluted leachate sample (COD = 3167 mg/L and NH_4-N = 144 mg/L) was subjected to three alternate adsorption treatments, using a stirred tank reactor of 1 L capacity and two adsorbent concentrations (10 and 30 g/L). The three adsorbents used were: (a) the rice husk powdered AC carbon (RH AC), (b) a commercial powdered AC from CPL Carbon Link (PAC) and (c) a zeolitised fly ash material (CV-Z), resulting from the alkaline activation of fly ashes from the Narcea Power Plant (Spain). The CV-Z product is composed of different zeolites (mainly Na-P1, and lower levels of analcime and chabazite) and the fly ash remaining after the alkaline activation [37]. The resulting suspensions were then stirred for 30 min at 150 rpm, and finally were settled for 4 h.

Samples of influent and effluent water were taken for analyses. Chemical oxygen demand (COD) and NH_4-N analyses were based on standard methods [38]. COD was carried out by the dichromate reflux method, whereas NH_4-N concentration was measured by using an ammonium ion selective electrode (Crison Instruments). Colour was determined by spectrophotometric method (measuring at 400 nm), which involves the prior filtration of the samples through 0.45 μm cellulose acetate filter. All the analyses were done in duplicate, taking the average of two values.

Table 2
Properties of the ACs used for the adsorption tests

	AC from rice husk	AC from sugarcane bagasse
S_{BET} (m^2/g)	811	864
Average pore diameter d_{av} (nm)	2.02	2.05
Pore volume (cm^3/g)	0.41	0.43
Micropore volume (cm^3/g)	0.42	0.44
Average particle size (nm)	41.21	54.87
Ash content (%)	27.8	40.6
pH	5.3	5.9

3. Results and discussion

3.1. *Single-stage production of ACs from rice husk and sugarcane bagasse*

The properties of the ACs that were prepared in single-stage chemical activation process are shown in Table 2. As indicated by the average particle size, the ACs are in powdered form. They have comparable values for their properties, the exception being the ash content, where the AC from rice husk and the AC from bagasse contain 27.8% and 40.6% ash, respectively. These ACs were used for the adsorption tests. As shown earlier, ACs with comparable surface area values, microporosity and ash content have yielded promising results with respect to arsenic, phenol, humic acid and landfill leachate adsorption [17–22,25–29]. Table 3 provides a summary of the activating conditions, surface area and total pore volume of the ACs prepared for this study, and of carbons from agricultural by-products reported in other papers.

3.2. *Adsorption of phenol*

As seen in Fig. 2, the adsorption isotherms of phenol on rice husk AC and bagasse AC, respectively, were favourable. Rice husk AC exhibited a higher adsorption capacity compared to bagasse AC, as indicated by the maximum loadings of 27.58

Table 3
Summary of optimal conditions for activation of various agricultural by-products

Material	Impregnating chemical	Activation temperature (°C)	Activation time (h)	BET (m2/g)	Total pore volume (cm3/g)	Reference
Rice husk	$ZnCl_2$	700	0.5	811	0.41	This work
Sugarcane bagasse	ZnCl2	700	0.5	864	0.43	This work
Pecan shells	H3PO4	450	1	1250		[63]
Olive stones	KOH	900	4	3049	1.52	[16]
Olive kernels	KOH	900	4	2159	–	[12]
Walnut shells	PO_4 salts	750	–	850	–	[64]
Hazel nuts	$ZnCl_2$	750	10	793	–	[65]
Peanut hulls	H_3PO_4	500	3	1177	0.57	[14]
Peach stones	$ZnCl_2$	850	–	3000	–	[15]
Corn cobs	KOH	850	1	2700	–	[66]
Olive seed waste	KOH	800	3	1690	0.9	[23]
Oak wood	–	900	–	684	0.45	[23]
Pine wood	–	900	2.5	896	0.61	[23]
Almond shells	H_3PO_4	450	1	1340	–	[21]
Olive stones	$ZnCl_2$	650	2	790.25	–	[24]
Oil palm shell	Steam	900	1	1183	0.69	[67]

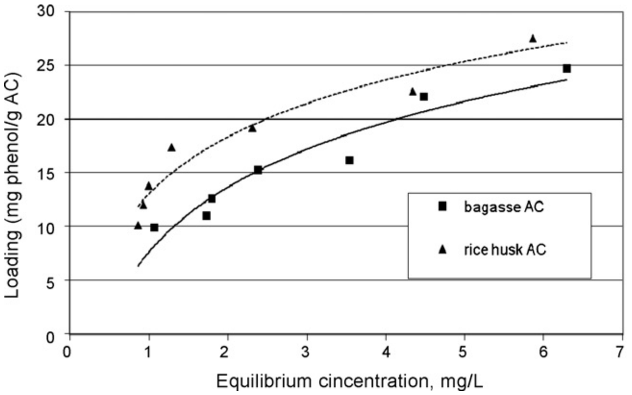

Fig. 2. Adsorption isotherms of phenol on rice husk and sugarcane bagasse activated carbons.

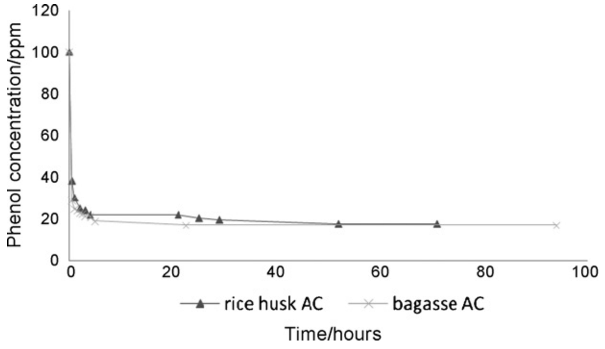

Fig. 3. Phenol kinetics for the rice husk and bagasse activated carbons.

and 24.68 mg phenol/g AC, respectively. The data were analyzed using the Langmuir and Freundlich model isotherms and the coefficients are shown in Table 4.

These results agree with those obtained by several researchers that observed favourable adsorption of phenol on ACs compared to other adsorbents such as peat, fly ash and bentonite [39–41]. Due to the microporous nature of our carbons, phenol, being a smaller size molecule, adsorbed better than HA. It is known that the rate of adsorption often depends on the diffusion coefficient, which is strictly associated with the molecular size of the adsorbate. Diffusion coefficients of HA and phenol are sufficiently different to ensure superior kinetics of the smaller compound [42,43].

In kinetic terms, it was found that the phenol–rice husk AC and phenol–bagasse AC adsorption system reached equilibrium in ∼4 h, as shown in Fig. 3. At this time, ∼80% of the initial phenol concentration was removed. This is comparable to the equilibrium times achieved by other researchers that used phenol and ACs in similar conditions. Zogorski et al. [44] observed that the adsorption of phenolic compounds by granular carbon was extremely rapid and within the first hour of contact, 60–80% of the ultimate adsorption could occur. Sachan et al. [45] also reported that within 2 h of adsorption time, about 80% phenol was adsorbed by AC. Our observations also agree with those of Jung et al. [46] that studied the adsorption behaviour of phenol and chlorophenols on several commercial ACs. They concluded that their adsorption was not affected by the physical properties of activated carbons but mainly by chemical interaction.

In a recent study, Mukherjee et al. [47] examined the adsorption of phenol on commercial AC, wood charcoal and bagasse ash. They used a phenol solution of 30–50 mg/L and adsorbent at 50 g/L. They concluded that wood charcoal and bagasse ash were comparable to commercial grade AC in the removal of phenol from water. Their experimental results showed that ca. 98%, 90% and 90% removal was achieved in 1 h by the commercial AC, the wood charcoal and the bagasse ash, respectively.

Similar results were obtained by Özkaya [48], who studied the adsorption and desorption of phenol on commercial activated carbon using 100 mg/L solutions. For the adsorption experiments, the AC dosage ranged from 0.05 to 0.9 g/100 mL. His results showed that after the equilibrium time of 2 h, 96% of phenol was removed from solution. Kennedy et al. [49] tested the phenol adsorption on AC prepared from rice husk in a two-stage process using H_3PO_4 as the impregnating agent. The optimum AC was obtained at 900 °C and had a surface area of 438.9 m^2/g. This AC showed the maximum phenol uptake at pH of 2.7. In our studies, the pH remained unaffected throughout the adsorption process.

Several researchers have investigated the effect of particle size on the equilibrium kinetics of phenol and agreed that the smaller the particle size the faster the diffusion of the phenol molecules [40,50,51,53]. Roostaei and Tezel [40] studied the

Table 4
Langmuir and Freundlich adsorption model coefficients

	Freundlich isotherm					
	K			1/*n*		
	Phenol	HA	Arsenic	Phenol	HA	Arsenic
Rice husk AC	0.4080	4.9496	0.8768	0.4303	0.1619	0.1433
Bagasse AC	0.3414			0.5435		
	Langmuir isotherm					
	a			*b*		
	Phenol	HA	Arsenic	Phenol	HA	Arsenic
Rice husk AC	19.455	333.33	3.795	1.8423	0.0005	0.228
Bagasse AC	12.33			2.4727		

removal of phenol from aqueous solution by adsorption on to various commercial adsorbents. They particularly examined the influence of the adsorbent particle size on the adsorption process and concluded that the particle size did not affect the capacity of adsorption, however, the adsorption kinetics got faster with decreasing particle size. Therefore, the smaller the particle size the faster is the diffusion of phenol into adsorption sites within the adsorbent. The fastest adsorption kinetics were exhibited by HiSiv 1000 (zeolite Y-structure), which had a particle size of 50 mesh × 70 mesh (212–297 μm). Using a 100 mg/L phenol solution (as in our case), equilibrium was achieved in 3 h, which is comparable to the 4 h achieved in this study.

Juang et al. [52] studied the liquid phase adsorption and desorption of phenol onto granular activated carbons (GACs) prepared from coconut shell. Their GACs had surface areas between 732 and 802 m^2/g, total pore volumes of 0.49–0.64 cm^3/g and average pore size ∼3.90 nm. Adsorption was tested on different AC particle sizes, ranging from 1.15 to 4 mm. The results showed that as the carbon particle size decreases, so does the diffusion path. Therefore, quicker equilibrium times were achieved, although the loading values remained very similar between the AC with different particle sizes. The equilibrium times achieved by Juang et al. ranged between 8 and 10 h whereas in this study equilibrium times were considerably lower (4 h). Since the GACs characteristics mentioned earlier are comparable to the values of our ACs, the longer equilibrium times can be attributed to the larger particle size of the GACs.

3.3. Adsorption of arsenic

The result of the arsenic adsorption on rice husk AC is shown in Fig. 4. The adsorption isotherm is favourable, showing a maximum loading of 1.22 mg As/g AC. This result essentially agrees with the findings of Diamadopoulos et al. [35], who studied the effect of AC properties on the adsorption of phenol, fulvic acid and arsenic. In the case of As, they showed that ACs with high ash content were able to remove up to 5 times as much As from water, compared to ACs without any ash. This was due to the high CaO and Fe_2O_3 content in the ash. Mohan and Pittman [53] reviewed the removal of arsenic from a wide range of adsorbents, such as commercial ACs, agricultural by-products, clay minerals and zeolites. They showed that ACs produced from agricultural wastes offered a low-cost, efficient alternative to commonly used arsenic adsorbents.

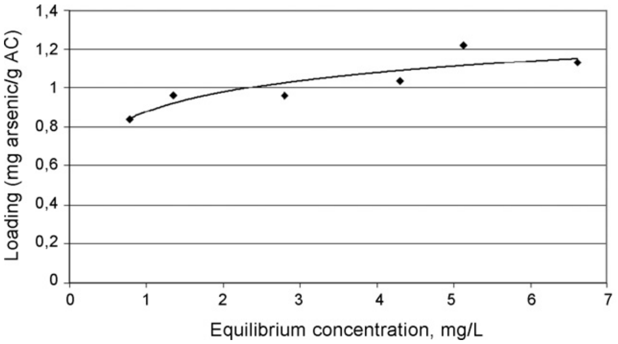

Fig. 4. Adsorption isotherms of arsenic on rice husk activated carbon.

Huang and coworkers [54,55] also studied the adsorption of As by commercial ACs and concluded that lignite-based ACs (which are characterized by high ash and CaO/Fe_2O_3 content) were more effective in removing As(V), from water as opposed to low-ash ACs. The predominant role of ash in arsenic adsorption by ACs was also confirmed by Lorenzen et al. [56]. They used a coconut-shell AC, a peat-based AC and a coal-based AC to adsorb arsenic and showed that the AC with the higher ash content (but not necessarily the largest surface area) exhibited the highest arsenic loading of 4.09 mg/g carbon.

These results indicate that there is a strong interaction between arsenic and mineral matter. Therefore, the ash content and the CaO and Fe_2O_3 percentages therein play a more important role in arsenic adsorption compared to the surface area [35,41]. Both the rice husk and sugarcane bagasse ACs have relatively high ash contents (27.8% and 40.6%, respectively); however, the CaO and Fe_2O_3 contents are very low (0.73% and 0.28% for rice husk and 2.73% and 1.19% for bagasse, respectively). This possibly accounts for the low As loading achieved in the rice husk AC. Since bagasse has comparable CaO and Fe_2O_3 contents to rice husk, and the AC produced from bagasse has very similar characteristics to the rice husk AC, we thought it would be redundant to perform arsenic adsorption tests on the bagasse AC. Table 5 shows a comparison of the RH AC with other carbons of similar surface area, with respect to As adsorption capacity.

3.4. Adsorption of humic acid

The adsorption isotherm shown in Fig. 5 is favourable exhibiting a maximum loading of 11.59 mg HA/g AC. The rice husk

Table 5
Comparison of the rice husk AC adsorption characteristics with other adsorbents, with respect to arsenic[a]

Adsorbent	Surface area (m^2/g)	Arsenic concentration (mg/L)	Capacity As(III) (mg/g)
RH AC used in this study	811	10	1.22
Activated alumina	370	1	0.18
Tea fungal biomass	–	1.3	1.11
$FeCl_3$ treated tea-fungal biomass	–	1.3	5.4
FeO_3 impregnated GAC	840	1	4.5
Olive-stone and olive pulp ACs	732–1850	5–20	0.21–1.39
Modified calcined bauxite	–	0.5–0.8	1.37
Goethite	12.7	10–1000	7.5

[a] Data obtained from Ref. [53].

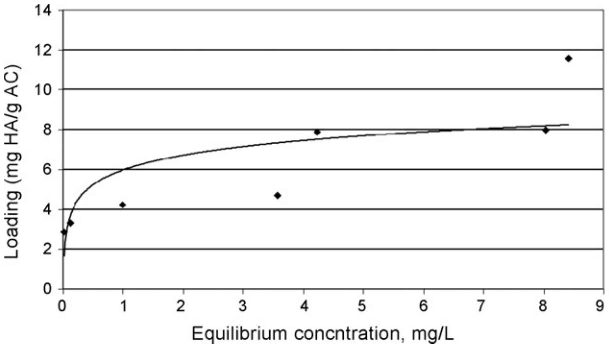

Fig. 5. Adsorption isotherm of humic acid on rice husk activated carbon.

AC behaved in a similar manner as in the case of As adsorption. The adsorption of humic acid is mainly determined by CaO and Fe_2O_3 content of the adsorbent [35] and the molecular size of the HA [57]. The low CaO and Fe_2O_3 of the precursor materials and the microporous nature of our carbons do not promote high HA adsorption. Han et al. [57] studied the adsorption of humic acids on two commercial microporous ACs and one mesoporous AC. They clearly showed that regardless of the surface area of the carbons and the pH conditions, the adsorption capacity of the mesoporous carbon was much higher than that of microporous carbons. At all the pH values they employed, the HA loadings for the microporous carbons did not exceed 20 mg/g, whereas the mesoporous carbon achieved a maximum loading of 100 mg/g.

Similar results were obtained by Lorenc-Grabowska and Gryglewicz [58], who studied the adsorption of HAs on coal-based mesoporous ACs. They found that as mesoporosity increased, so did the percentage removal of HAs. Since the ACs used in this study were basically microporous, the low removal percentages of HA from solution were rather expected. This observation was also confirmed by Tomaszewska et al. [59] who studied the removal of organic matter by coagulation enhanced with adsorption on powdered activated carbons. Daifullah et al. [60] studied the factors affecting the removal of HA by AC prepared from rice husk impregnated with H_3PO_4. They found that acidic oxides such as SiO_2 and P_2O_5 (commonly present in ash) enhance the adsorption of HA by lowering pH. For the same reasons as in the case of arsenic, humic acid adsorption on bagasse AC was not performed.

3.5. Activated carbon treatment of a landfill leachate

Fig. 6 shows the results obtained when the landfill leachate was treated by the three different adsorbents. The percentages of COD removal obtained with CV-Z were very low, both for 10 and 30 g/L of CV-Z used, reaching values of 5% and 14%, respectively. These results are in agreement with those obtained in a previous work [61] using physico-chemical-adsorption treatment. However, the RH AC treatment achieved a COD removal of 34% and 70% for the same concentrations. Rodriguez et al. [62] used a granulated AC with a surface area of 1000 m^2/g and three resins to remove COD from landfill leachate. Of the four adsorbents, the AC showed the highest COD removal, reducing the COD level from 1300 to 200 mg O_2/L after 2 h of contact, which corresponds to a reduction of 85%.

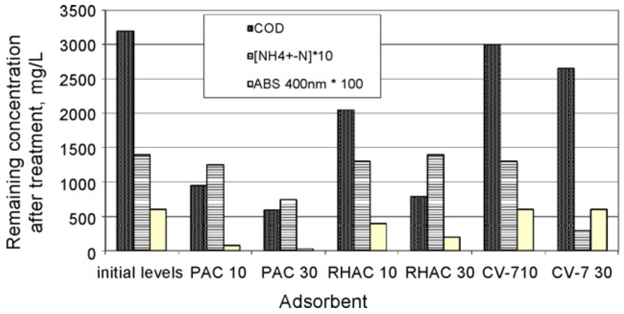

Fig. 6. Landfill leachate treatment using a commercial activated carbon (PAC), a rice husk activated carbon (RH AC) and a zeolitised fly ash material (CV-Z).

Regarding NH_4-N, CV-Z removed just 10% at 10 g/L, but at 30 g/L the removal of ammonium-N significantly increased to 74%. CV-Z did not remove any colour. The colour of the leachate was efficiently removed using PAC at 30 g/L under the same conditions. Removal efficiencies obtained were 79% and 98%, for 10 and 30 g/L of PAC, respectively. The RH AC removed 31% and 60% of colour when 10 and 30 g/L were used, respectively. Therefore, RH AC showed at 30 g/L a similar adsorption capacity to the commercial AC in the case of COD.

4. Conclusions

The production of added value products such as ACs from biowaste is very important from both environmental and economical scope. In developing countries, the majority of rice husk and bagasse are used as an alternative energy source to fossil fuels. Despite the wide consumption of bagasse and rice husks as a fuel for the mill boilers, for electricity and steam generation, animal feed or as a raw material for the manufacture of paper and board, the residues still remain as a surplus which poses a disposal problem for mill owners. The processing and transformation of agricultural residues into activated carbon with good adsorption properties would alleviate problems of disposal and management of these waste by-products, while providing a high-quality end product for water and wastewater treatment that could potentially expand the carbon market.

Our results showed that the ACs prepared from rice husk and sugarcane bagasse had good adsorption capacities with respect to arsenic, humic acid and phenol. They removed ∼80% of phenol at the equilibrium time of 4 h. Regarding the study on the treatment of landfill leachate using the powdered activated carbon, the results showed that, with 30 g/L of AC it was possible to remove 70% and 60% of COD and colour, respectively. Therefore, this material may be suitable in pre- or post-treatment steps of landfill leachate, in combination with other processes in order to meet regulatory limits.

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