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## Biosorption of model pollutants in liquid phase on raw and modified rice husks

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**Abstract.** We studied the application of rice husk (RH) as a biosorbent and we demonstrated that it can be employed for the treatment of dyeing wastewater streams. RH was obtained from Nile Delta (Egypt) and it was used as received, or after a chemical treatment using HNO<sub>3</sub> or NaOH, or after conversion into activated carbon (RH-AC) using H<sub>3</sub>PO<sub>4</sub> as activating agent. A commercial activated carbon GAC 830 provided by NORIT was also tested for comparison purposes. These materials were evaluated by adsorption of methylene blue (MB) with an initial concentration of 20 ppm in an aqueous solution at 30°C. The results showed that alkali-treated and RH-AC were the best sorbents. They got a nearly complete MB removal from water and they had better performance than GAC 830. Therefore, the use of RH for pollutant removal makes this method an environment-friendly option and an economically feasible alternative to treat industrial effluents.

### 1. Introduction

Rice husk (RH) is a by-product of the milling process of rice crop which is widely cultivated in the world. RH contains suitable characteristics for some pollutant adsorption and it could be discharged as agricultural waste [1]. The major components of RH which may be responsible for sorption are carbon and silica: the former for its high surface area and pore volumes, and the latter for its interaction with organic polar compounds [2, 3].

Different methods can be used for the removal of organic compounds and dyes from wastewater streams. The conventional treatment processes, such as coagulation, sedimentation, and filtration are less effective in removing organic molecules [4, 5]. Biological treatment (aerobic and anaerobic) can reduce organic matter and the type of treatment applied to sludge is usually chosen depending on its nature and environmental factors. However, several technological changes in the system are needed in order to decrease the concentration of some persistent organic pollutants. Therefore, it seems that the adsorption method is the most effective and economically feasible alternative for the removal of organic pollutants [6, 7].

Adsorption on indigenous materials is a relatively simple and low-cost method for the treatment of industrial and domestic effluents. Few studies examined the utilisation of rice by-products for organics adsorption, such as: rice bran being a potent sorbent for the removal of organochlorine compounds and

benzene from industrial wastewaters; use of river sand for sorption of Cd (II) from aqueous solutions and also use of rice husk ash for preconcentration of gold [2] and therefore it seems that rice husk is a promising agricultural waste material to be implemented in the wastewater treatment systems.

## 2. Experimental

### 2.1. Preparation of treated rice husk and characterisation of natural RH

RH was used without any modification as biosorbent. RH was also treated with  $\text{HNO}_3$  (RH- $\text{HNO}_3$ ) and NaOH (RH-NaOH). We prepared RH- $\text{HNO}_3$  as follows: 250g of RH were soaked in 1L of  $\text{HNO}_3$  2M, left for 2 hours at room temperature and then washed with distilled water using a Soxhlet extractor. Finally, it was dried in an oven at  $60^\circ\text{C}$  for 24 hours. RH-NaOH was prepared as follows: 300g of RH was soaked with 1L of NaOH 1.5% and left for 2 hours at room temperature. After that, the mixture was transferred to an autoclave at  $121^\circ\text{C}$  during 30min and then washed using Soxhlet extractor. Finally, the material was dried in an oven at  $60^\circ\text{C}$  for 24 hours.

The proximate characterisation of the natural RH included the percentage of cellulose, hemicellulose, lignin, ash and moisture content. For the determination of lignin, the Klason method [8] was used. The ash content was determined by weighing up natural RH before and after being burnt in a muffle oven at  $600^\circ\text{C}$  following the standard procedure (ASTM D 1102-84). All the samples were weighed before and after being placed in an oven for 4 hours at  $105^\circ\text{C}$  for the determination of moisture.

### 2.2. Preparation of activated carbon from rice husk and characterisation of ACs

A series of experiments were carried out to optimize the orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ) activation conditions and the results showed that the optimal conditions, in relation to textural properties (surface area and microporosity) were: temperature of  $425^\circ\text{C}$ , activation time of 30 min; and impregnation weight ratio ( $\text{H}_3\text{PO}_4/\text{RH}$ ) of 1.2. The mixture was kept one hour for impregnation and introduced into a vertical oven for activation. The mixture was placed in the thimble to be washed with water for five days using a Soxhlet extractor.

The specific surface areas ( $S_{\text{BET}}$ ) of the commercial activated carbon (GAC 830) and the activated carbon prepared from rice husk (RH) and porosity were determined by  $\text{N}_2$  adsorption at 77 K with an automatic instrument Micromeritics - ASAP 2020. The samples were analysed according to the BET method for calculating the specific surface area and the Dubinin-Radushkevich (DR) method [9] was used to calculate the micropore volume,  $V_{\text{micro}}$ . The total pore volume,  $V_{0.99}$  was calculated from  $\text{N}_2$  adsorption at a relative pressure of 0.99. The mesopore volume,  $V_{\text{meso}}$ , was calculated by the difference between  $V_{0.99}$  and  $V_{\text{micro}}$ . The percentage of ash content and humidity was determined following the ASTM (D 2867-04) standard.

### 2.3. Adsorption experiments

*2.3.1. Kinetic study.* Adsorption kinetics were studied by mixing 500 mg of AC (NORIT GAC 830, RH-AC) or 2.5 g of biomass (RH-AC, RH- $\text{HNO}_3$ , RH-NaOH or raw RH) with 500 mL of solutions containing 20 ppm of methylene blue (MB). The mixture was then put in a thermal bath with water temperature set at  $30^\circ\text{C}$  [10,11] and stirred till reaching the adsorption equilibrium.

*2.3.2. Adsorption isotherms.* We determined the MB adsorption isotherms onto the 5 aforementioned materials. We used glass tubes containing 10 mL of 20 ppm of MB solution and we added between 1 and 35 mg of sorbent. The tubes were closed and put in the thermal bath under stirring at  $30^\circ\text{C}$  for approximately 8 hours. The MB residual concentration was measured by UV spectrophotometry and in order to describe the adsorption data, three well-known mathematical equations, namely: Freundlich, Langmuir and Temkin were tested. The main difference between those three models is basically the way the heat of adsorption decreases with the surface coverage. Langmuir assumes no

decrease at all, Freundlich assumes a logarithmic decrease, while Tempkin assumes a linear decrease [12, 13].

### 3. Results and Discussion

#### 3.1. Characterisation of natural RH

Proximate analysis results of the raw RH were: 35% of cellulose; 21% of hemi-cellulose; 20% of lignin; 19% of ash and 5% of humidity, in good agreement with other authors [1, 15].

#### 3.2. Characterisation of ACs

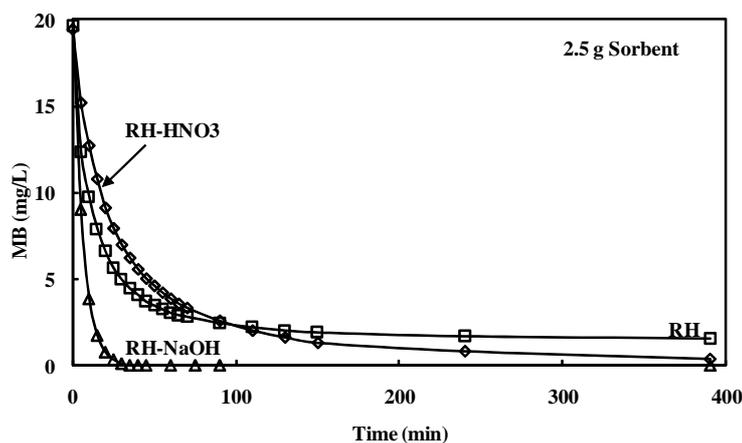
Table 1 contains the following values for the two activated carbons:  $S_{BET}$ ,  $V_{0.99}$ ,  $V_{micro}$ ,  $V_{meso}$ , % of moisture and ash content. The surface area ( $976 \text{ m}^2/\text{g}$ ) and the corresponding micropore volume ( $0.35 \text{ cm}^3/\text{g}$ ) are higher for the commercial activated carbon comparing to the RH:  $717 \text{ m}^2/\text{g}$  and  $0.25 \text{ cm}^3/\text{g}$ , respectively. Whereas the RH-AC presents higher mesopore volume ( $0.41 \text{ cm}^3/\text{g}$ ) compared to GAC 830 ( $0.21 \text{ cm}^3/\text{g}$ ) as it can be seen in table 1.

**Table 1.** Textural parameters, moisture and ash content of the ACs.

	$S_{BET}$ ( $\text{m}^2/\text{g}$ )	$V_{0.99}$ ( $\text{cm}^3/\text{g}$ )	$V_{micro}$ ( $\text{cm}^3/\text{g}$ )	$V_{meso}$ ( $\text{cm}^3/\text{g}$ )	Moisture (%)	Ash (%)
<b>GAC 830</b>	976	0.56	0.35	0.21	1.6	8.0
<b>RH-AC</b>	717	0.66	0.25	0.41	1.0	31.4

#### 3.3. MB adsorption kinetics

Figure 1 shows that MB concentration first rapidly decreased and then remained almost constant. RH-NaOH reached in less than 1 hour MB adsorption equilibrium and MB removal was complete. RH and RH-HNO<sub>3</sub> reached the equilibrium after 2 hours and MB was not completely removed from aqueous solution.

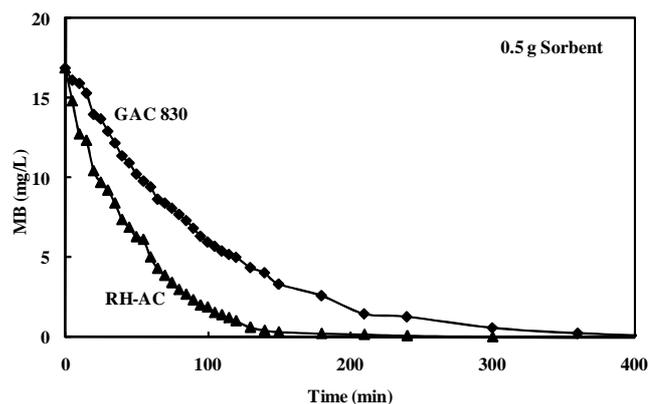


**Figure 1.** Decrease of MB concentration with time for the 3 sorbents studied:  $\Delta$  RH-NaOH,  $\diamond$  RH-HNO<sub>3</sub> and  $\square$  RH. ( $C_0=20 \text{ mg/L}$ ,  $V= 500 \text{ mL}$ ,  $2.5\text{g}$  of sorbent,  $T=30^\circ\text{C}$ ).

#### 3.4. Kinetics for MB removal using ACs

Figure 2 shows the performance of the two ACs, GAC 830 and AC-RH, for MB removal. Adsorption studies clearly indicated that the RH-AC possesses excellent adsorption characteristics and has the potential to be used for the removal of dyeing basic compounds. Both ACs are able to remove 100% of MB from aqueous solution but RH-AC reached the equilibrium much faster than GAC 830, approximately in 2 h compared to GAC 830: around 6 h.

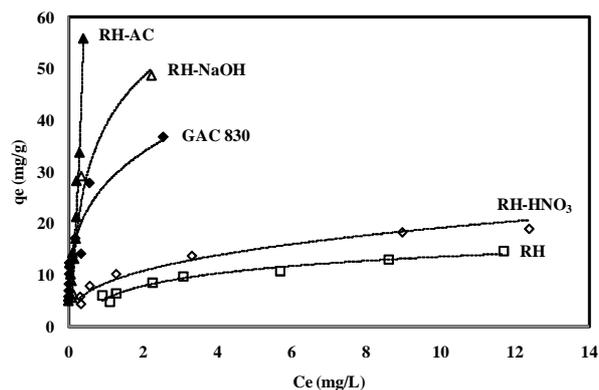
The main explanation for finding great adsorption capacity of MB onto activated carbon materials with lower surface areas and microporosity may be the size of molecule which is around 1.5 nm, so this compound is adsorbed only in large micropores and mesopores (>2 nm). Furthermore, the higher uptake capacity may be explained by the surface chemistry of the RH-AC (pH equal to 2.53). MB has a basic character and when it is put in contact with the strong acidic surface of RH-AC, electrostatic interactions occur between electrons from the carbon surface and the dye molecule favouring the adsorption mechanism [4, 12].



**Figure 2.** Decrease of MB concentration with time for the 2 ACs studied:  $\blacktriangle$  RH-AC and  $\blacklozenge$  GAC 830. ( $C_0=20$  mg/L,  $V= 500$  mL, 0.5g of sorbent,  $T=30^\circ\text{C}$ ).

### 3.5. Adsorption isotherms

Figure 3 shows MB adsorption isotherms onto the 5 materials tested. RH-AC showed the highest and RH the lowest MB adsorption for the same concentration at equilibrium. RH-NaOH demonstrated also to be a very good adsorbent and it had better performances than the commercial AC, GAC 830.



**Figure 3.** MB adsorption isotherms onto:  $\square$  RH-NaOH,  $\diamond$  RH-HNO<sub>3</sub>,  $\square$  RH,  $\blacktriangle$  RH activated and  $\blacklozenge$  GAC 830. ( $C_0=20$  mg/L,  $T=30^\circ\text{C}$ ).

Table 2 shows the maximum uptake per unit mass of sorbent,  $q_m$ , determined by the application of Langmuir model. These data confirm that RH-AC had the best performances for MB adsorption using only 0.5 g of ACs compared to 2.5 g of treated and raw RHs.

**Table 2.** Maximum uptake per unit of adsorbent,  $q_m$ , derived from application of Langmuir's model

Sorbent	$q_m$ (mg/g)
RH	16.9
RH-HNO <sub>3</sub>	20.8
RH-NaOH	71.4
GAC 830	83.3
RH-AC	217.4

#### 4. Conclusions

RH can be employed efficiently for the removal of basic dyes after NaOH treatment: RH-NaOH, or after H<sub>3</sub>PO<sub>4</sub> activation: RH-AC. For biosorbents, the order in MB adsorption efficiency was RH-NaOH (71.4 mg/g) > RH-HNO<sub>3</sub> (20.8 mg/g) > RH (16.9 mg/g). RH-AC showed better performances as adsorbent for MB (217.4 mg/g) than the commercial GAC 830 (83.3 mg/g); this is probably due to the higher mesoporosity and more acidic character of RH-AC. Taking into account the activation costs, RH-HNO<sub>3</sub> is probably the most economical sorbent for MB removal.

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