

Humic Substance Bioremediation Using Biomass Agricultural Waste: Process and Mechanism

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Abstract: A biomass agricultural waste material, Rice Straw was used for preparation of activated carbons by physical activation and modified with KOH (RSK carbon). Bioremediation of Humic Substance (HS) by RSK carbon was investigated through equilibrium process. The experimental results showed that the equilibrium data fit well Langmuir equation. It was found that for RSK carbon can achieve adsorption of HS at 21.1 mg g⁻¹. The underlying mechanism of HS sorption was discussed. It could be concluded that A mixed effect of electrostatic attraction and surface complex formation is suggested to be responsible for the adsorption of humic substance on the surface of carbon.

Key words: Bioremediation, biomass, humic substances, carbon, adsorption

INTRODUCTION

Humic Substances (HS) are one of the most important groups of naturally occurring biomolecules (Daifullah *et al.*, 2007) and do not belong to any unique chemical category. Humic substance are formed by the biological decomposition of plant and animal matter in the environment. Rainwater carries these molecules through the soil and eventually into creeks, rivers and reservoirs. Humic substances are present in natural surface waters in concentrations from several tens to about 120 mg L⁻¹. They have an undesirable effect on the appearance and taste of water. The concentration of HS in drinking water must be very low for their negative effects on human health. HS are able to bind heavy metals and to adsorb hydrophobic toxic molecules they may therefore facilitate the diffusion of these contaminants (Heinen *et al.*, 2000).

A relationship between HS in drinking water and some endemic diseases (e.g., chronic osteoarthritis and peripheral vascular disorder) has been reported (Heinen *et al.*, 2000). Moreover, the treatment of HS-containing water with chlorine may result in the formation of trihalomethanes (THMs) that is a known human carcinogen (Shim *et al.*, 2001).

Moreover, the presence of humic substances is very detrimental in water treatment processes. In commonly employed procedures, increased contents of these substances can lead to a number of problems¹. The treatment of HS-containing water with chlorine may result

in the formation of Trihalomethanes (THMs) (Shim *et al.*, 2001) that is a known human carcinogen (Shim *et al.*, 2001). Ozonation can also lead to release of some pesticides or heavy metals formerly bound in humate complexes.

Many techniques are used in waterworks for the abatement of HS, coagulation and interaction with insoluble materials by anion exchange being the most commonly used methods. Removal of HS by modified granular activated carbon (Leon *et al.*, 1992) soluble cationic polyelectrolytes (Bandosz *et al.*, 1992) and metal-modified silica gels 2 have also been reported. However, active carbon is still best.

This study presents data and discussion regarding adsorption of humic substances on activated carbon-prepared from locally available material (Rice Straw).

MATERIALS AND METHODS

Activated carbon preparation and characterization:

Activated carbon was prepared according to procedures described by one of the researchers (Daifullah *et al.*, 2007). Briefly, 0.5 kg dried rice straw was fed into fluidized bed reactor at heating rate 5°C min⁻¹ under inert environment of nitrogen at flow rate of 300 mL min⁻¹. when temperature reached 350°C, steam was introduced to the reactor at rate of 5 mL min⁻¹. Heating continued up to 550°C and hold for 1.0 h. The produced carbon was

treated with KOH to produce a modified carbon denoted as RSK, according to the procedures described earlier (Heinen *et al.*, 2000; Shim *et al.*, 2001).

The surface area and pore characteristics of the prepared carbons were determined by nitrogen adsorption at 77 k using Quantachrome Instruments, Model Nova1000e series, USA. Simple mass titration method was used to estimate the pH_{zpc} of carbons as reported 4. The Boehm titration Method was used to estimate the acidic and basic properties of carbons 5.

Sorption investigations: The stock solution of humic acid (Fluka) was prepared by dissolving the required amount of HS (sodium salt) in a least amount of distilled water, then transferred to 100 mL volumetric flask and completed to the mark with distilled water. Various fresh standard solutions were obtained daily as required.

Batch sorption studies were performed to study the efficiency of activated carbon in removal of HS from wastewater. Known amounts of RSK (5-160 mg) were added to 10 mL of 100 mg L⁻¹ HS solution followed by agitation for 24 h using thermostatic shaker (Kottermann D-1362, Germany) water bath at 25±1°C. Then the supernatant was filtered through Whatman No. 42 filter study and aliquots of filtrate were analyzed for the concentration of HS remaining in the solution. Blank tests were performed without activated carbon to confirm that precipitation had not occurred during the period of investigation.

The concentrations of HS in solutions were determined by measuring the absorbance with Shimadzu model 160A double-beam UV spectrophotometer at λ = 420 nm. The amount of metal ion sorbed on sorbent was calculated by (Metwally *et al.*, 2011):

$$q_e = \frac{V(C_o - C_e)}{m} \quad (1)$$

Sorption efficiency based on the percentage of metal removal:

$$R\% = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Where:

C_o and C_e = The initial and equilibrium concentration (mol L⁻¹), respectively

m = The mass of dry carbon sample used

(g) and V = The volume of solution (l)

RESULTS AND DISCUSSION

Modification of the surface chemistry of porous carbons might be a viable attractive route toward novel applications of these materials. Surface area of the

prepared carbon was lower than for the commercial carbons. Therefore, researchers conduct a surface modification for these carbons to obtain the highest adsorption capacity. The main physicochemical characteristics of RSK carbon were given in Table 1. It is clear that RSK carbon has more mesopores than micropores. Mesopores volume is three times greater than micropores volume. This good for the carbon as it was reported that the carbon mesopores enhanced its adsorption capacity for metals. The high ash contents of RSK carbon (50%) can be explained by consumption of a considerable amount of carbon during activation which leads to high specific mineral content, especially its richness in silica. The results in Table 1 show the coexistence of acidic and basic surface sites in RSK carbon that indicate its amphoteric behavior. KOH treatment results the appearance of surface oxygen groups like hydroxyl, carboxyl as indicated from IR analysis in Fig. 1. Bands around 2300 cm⁻¹, perhaps due to ketene or ketone. The band in the region of 1600 (1580 cm⁻¹) due to highly conjugated carbonyl groups. The 1420 cm⁻¹ band attributed to lactone structure. The 1100 cm⁻¹ peak corresponds to C-O stretching vibration and O-H bending modes of alcoholic, phenolic and carboxylic groups. Studies of uranium removal by RSK carbon showed that adsorption was maximum at PH 5.5 and equilibrium time of 40 min with equilibrium adsorption capacity 100 mg g⁻¹. The values of adsorption capacity for the removal of U(VI) were reported to be 58.43, 18.72, 28.49 and 28.30 mg g⁻¹ onto mesoporous silica (Stomberg *et al.*, 2003) diarylazobisphenol modified carbon (Starvin *et al.*, 2004) modified carbon (Kutahyali and Merl, 2004) and activated carbon (Mallah *et al.*, 2006) respectively. Therefore, it was clear that RSK carbon is more effective for this purpose. As a continuation of this research this study focused on the sequential and simultaneous adsorption of uranium and humic acids on RSK carbon.

Table 1: Characterization of RSK carbon

Parameters	Values
SBET m ² /g ^a	143.3
Surface area fraction ^b	
Micro-	0.7
Meso-	0.3
Total pore volume (cc g ⁻¹)	0.175
Pore volume fraction ^b	
Micro-	0.25
Meso-	0.75
Pore radius, nm	2.45
Basicity meq g ⁻¹	10.1
Acidity meq g ⁻¹	5.95
pHpzc	10.25
Ash content %	50.5

^aThe specific surface area calculated with the Brunauer-Emmett-Teller (BET) model; ^bThe surface area or pore volume fraction in each pore size range obtained from the Density Functional theory (DFT) analysis

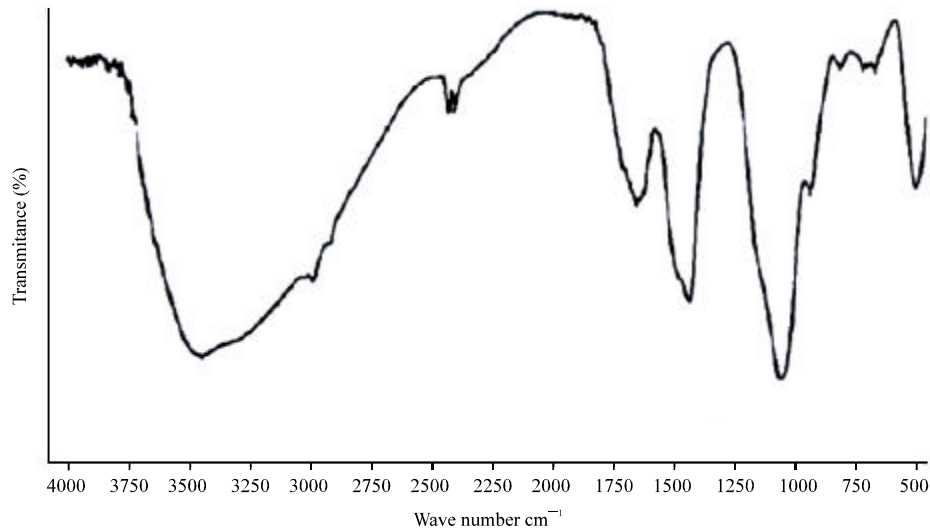


Fig. 1: FTIR spectra of RSK carbon

Sorption of humic substances: Humic Substance (HS) are polyelectrolytic macromolecules that are widely distributed in natural waters. It is well known that humic substances possess a substantial capacity to complex dissolved species such as metal ions. Their role in natural waters has gained importance because of these interactions that control the behavior and the mobility of metals. However adsorption of humic substances by activated carbon is of particular interest as they may significantly change the surface properties in general and surface charge in particular.

The adsorption isotherm of humic substances on RSK carbon at pH = 5.5 (optimum pH of single uranium adsorption onto RSK carbon) was given in Fig. 2. The isotherm showed an initial steep slope at low concentrations and then reached a plateau at elevated HS concentrations. The increase in the slope of the adsorption isotherms at low concentrations indicating a relatively high affinity between HS and carbon surface due to the number of reactive functional groups involved in the binding between them. Similar results were obtained by other researchers studying the sorption of humic substances onto aluminum and iron oxide surfaces (Parfitt *et al.*, 1977). In this concern, Ochs (Ochs *et al.*, 1994) proposed that polydispersity of humic substance was partly responsible for the initial fast sorption.

The equilibrium data were analyzed by the most commonly used isotherm: Langmuir and Freundlich models. Langmuir isotherm model suggests monolayer sorption on a homogeneous surface without interaction between sorbed molecules. This model assumes that adsorption occurs at specific homogeneous adsorption sites within the adsorbent and intermolecular forces

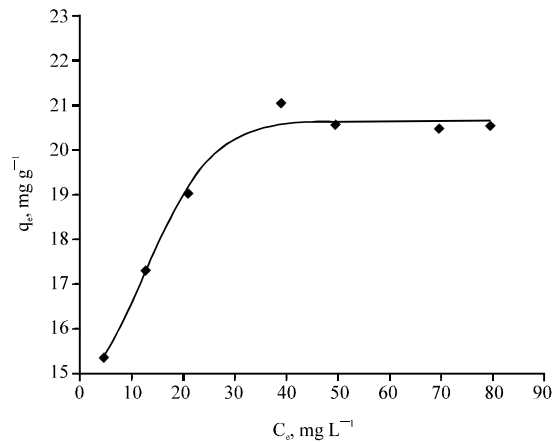


Fig. 2: Equilibrium sorption isotherm of Humic substance adsorption onto RSK carbon

decrease rapidly by the distance from the adsorption surface, linear form of Langmuir equation can be represented as (Aytas *et al.*, 2011):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (3)$$

Where

- q_e = The amount of HS sorbed onto the sorbent
- C_e = The equilibrium concentration of HS in solution
- Q_0 and b = Langmuir constants related to sorption capacity and sorption energy, respectively

Maximum sorption capacity (Q_0) represents monolayer coverage of sorbent with sorbate and b represents free energy of sorption and should vary with

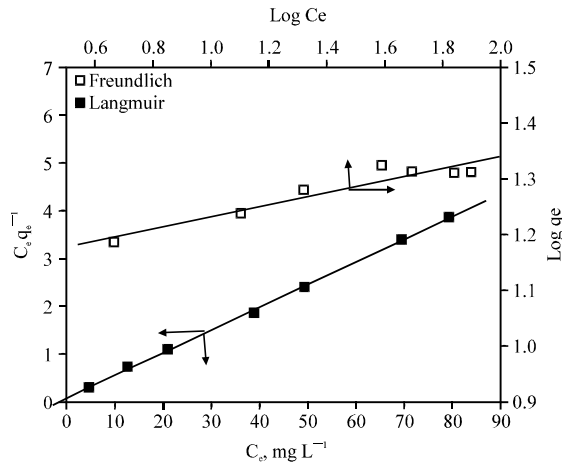


Fig. 3: Freundlich and Langmuir adsorption isotherms of Humic substance onto RSK carbon

Table 2: Freundlich and Langmuir Parameters for adsorption of Humic substance onto RSK carbon

Isotherm	Parameters	Values
Freundlich	K, mg g ⁻¹	13.30
	n	9.30
	R ²	0.90
Langmuir	Q ₀ , mg g ⁻¹	21.14
	b, L mg ⁻¹	0.53
	R ²	0.99

temperature. Q₀ and b were calculated from the slope and intercept, respectively of linear plots of C_e/q_e versus of C_e as presented in Fig. 3 and their values are listed in Table 2. Freundlich isotherm Model is an empirical relationship describing the sorption of solutes from a liquid to a solid surface and assumes that different sites with several sorption energies are involved, (Aytas *et al.*, 2009) which linear equation is given as the following (Aytas *et al.*, 2009):

$$\log q_e = \frac{1}{n} \log C_e + \log k \quad (4)$$

Where:

k = Constant which is an indicator to adsorption capacity at unit concentration

n = Exponent constant related to the adsorption intensity or bond distribution. if 1/n < 1, the bond energy increases with surface density, if 1/n > 1, bond energy decreases with surface density and for 1/n = 1, all surface sites are equivalent (Janardhana *et al.*, 2007).

The plot of log q_e against log C_e is illustrated in Fig. 3 and the Freundlich parameters, from the slope and the intercept are listed in Table 3.

From the fitting parameters in Table 2, it is clear that HS adsorption on RSK carbon were fitted much better to Langmuir adsorption model with regression coefficient (0.99) than Freundlich adsorption Model (0.9). The results also suggested the homogeneous adsorption sites in the adsorbents for HS adsorption. RSK carbon has point of zero charge (pH_{pzc}) of 10.25. It has a negative charge above the pH_{pzc} and a positive surface charge below the pH_{pzc}. As the HS quickly saturate the more energetic sites of carbon, fewer active sorption sites are available and/or the affinity of remaining HS to carbon surface became less due to the fractionation, resulting in a Langmuir-type isotherm. As anticipated, the large HS molecules will be adsorbed essentially on the external surface or in wider pores and thus upon covering the surface a second layer is not favorable. The HS molecules will favorably go into solution instead of forming a second layer over the already adsorbed layer (Daifullah, 2003). This observation is similar to that reported by Chen *et al.* (2004). Also, RSK carbon gave adsorption capacity of 21.1 mg g⁻¹ for HS which is similar to the adsorption of HS by unburned carbons separated from coal fly ash and treated by the same chemicals, KOH (Wang *et al.*, 2009). However, RSK carbon exhibits lower adsorption capacity for HS than other reported activated carbon adsorbents (Daifullah *et al.*, 2004; Wang and Zhu, 2007; Terdkiatburana *et al.*, 2008). This can be related to higher presence of acidic function groups on RSK carbon (Wang *et al.*, 2009). Also as the pH of the solution increases, the HS may become less compact and more separated owing to increased electrostatic repulsion, resulting in an overall decrease in adsorption capacity (Joseph *et al.*, 2012).

Sorption mechanism: The HS adsorption is dependent on the chemical and physical properties of both HS and activated carbons. Humic substance contains several functional groups, COOH, OH and NH₂ as shown in Fig. 4. In addition, the oxygen functional groups on RSK carbon play an important role in adsorption. The adsorption of HS on RSK carbon can be attributed to physisorption/chemisorption. In general, due to extremely complex composition of HS, multiple mechanisms such as electrostatic interactions, hydrogen bonding and π-π interactions can be involved in their sorption by RSK carbon. Activated carbon contains delocalized π electrons on graphene, showing the electron-donor property (Lavrinenko-Ometinskaya *et al.*, 1989). In aqueous solution, proton complexation of the π electron system of graphene will occur and acts as Lewis basic sites which will be responsible for adsorption of the negative charge species of COOH and OH in humic substance by electrostatic attraction. Hydrogen bond was another

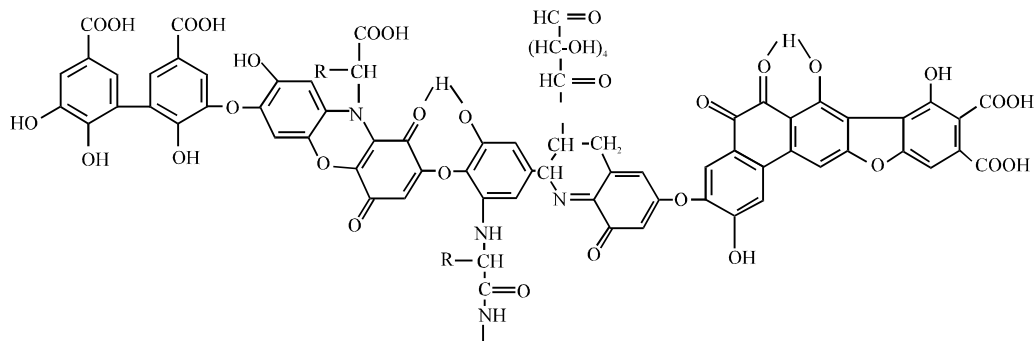


Fig. 4: Model structure of Humic substance

mechanism for the adsorption of HS on RSK carbon. The OH and COOH groups on RSK carbon will also be chemically bonded with amino (NH₂) and several hydroxyl groups (OH) in humic substance by forming strong hydrogen-bonding interaction, resulting in further higher adsorption. The π - π interactions has been proposed as an important mechanism for the adsorption of aromatic chemicals on carbon-based materials (Liu F-f *et al.*, 2013). HS molecules were rich in aromatic moieties which were theoretically able to interact with the electron-rich sites at the graphene surfaces of carbon via π - π interactions, thereby enhancing their sorption.

CONCLUSION

Activated carbon was successfully prepared from rice straw by steam pyrolysis and modified by KOH to give RSK carbon which used for the sorption of HS. The experimental results showed that the equilibrium data fit well Langmuir equation. The electrostatic attraction and surface complex formation are responsible for the adsorption of HS on the carbon surface.

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