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Sorption of Simulated Biomass Gasification Wastewater on Rice Husk Char and Activated Carbon

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Abstract

Biomass gasification using wood and rice husk as fuel is gaining popularity as an energy source in rural areas. However, the wastewater produced during gas clean-up may cause contamination of ground water and surface water if discharged without adequate treatment. The wastewater is characterized by presence of hazardous organic compounds, such as phenolics, monoaromatics, polynuclear aromatic hydrocarbons and heterocyclics. This study was designed to evaluate the potential of using sorption process for treating gasifier wastewater and to determine if rice husk char (RHC), a by-product in the gasification process may be utilized as a sorbent. Sorption on RHC was compared to sorption on activated carbon (AC) which is commonly used for water treatment applications. Batch sorption studies were conducted using a simulated biomass gasifier wastewater with ten components, characterized by chemical oxygen demand (COD), and phenolics of 2343 ± 53 and 772 ± 10 mg/L, respectively. Kinetic studies revealed that equilibrium was achieved within 12 h. Reduction of total organics due to sorption on AC depicted a distinct biphasic profile with a rapid phase followed by a slow phase. At a sorbent dose of 10 g/L, RHC could remove only 20 ± 1.4% of total organics (COD) and 21 ± 3.5% of phenolics from simulated wastewater whereas the removals with AC were 83 ± 4% and 91 ± 0.6%, respectively. The kinetic data fitted with the pseudo-first order model and intraparticle diffusion model indicated faster sorption on AC compared to RHC. The Langmuir model could not be applied for sorption of organics on AC and RHC. Moreover, for all other scenarios, although the R^2 values based on linearized model fits were in the range of 0.73-0.90, the isotherm plots for loading on sorbent versus aqueous phase concentration at equilibrium, revealed poor fits to experimental data.

Keywords: Gasifier wastewater; rice husk char; activated carbon; adsorption; rice husk.

1. Introduction

There is much interest in development and installation of biomass gasifiers in rural India for meeting the thermal and electrical energy requirements in a cost effective manner. However, sustainable use of gasifiers would require characterization and proper treatment of the waste streams before they are released into the environment. Wastewater gets generated when wet cleaning technology is adopted for producer gas clean-up. Since the composition of producer gas and tar varies with variation in the source of biomass used for energy generation (wood, coconut shell and agricultural byproducts), scale of operationand gasifier type (up-draft or down-draft), the wastewater characteristics are also highly variable (Jeswani and Mukherji, 2012). The chemical oxygen demand (COD) of this wastewater is reported to vary from 920 mg/L to 160,000 mg/Ldue to presence of organic contaminants (Jeswani and Mukherji, 2013).Recalcitrant organic contaminants, such asphenolics, polynuclear aromatic hydrocarbons (PAHs) and heterocyclic compounds, (Tian et al., 2006) known to possess toxic, mutagenic and carcinogenic properties are present in the wastewater (Jansen et al., 2002). Although biological treatment of this wastewater has been shown to be feasible through bioaugmentation with specific microorganisms (Jeswani and Mukherji, 2012 and 1013; Tian et al., 2006), the residual concentration of organic contaminants that remain undegraded may still pose a risk due to the chronic toxicity posed by the contaminants. Adsorption processes, employing sorbents such as activated carbon may be used for post treatment of this wastewater.

Although there are many studies on removal of phenol on activated carbon (AC) prepared from various low cost/agro- waste materials (Lin and Juang, 2009; Rengaraj*et al*., 2001; Achak*et al*., 2008), there is only limited literature on removal of phenolics from complex wastewater through adsorption. Mehta and Chavan (2009) demonstrated good removal of phenolics from a wood-based biomass gasifier wastewater. Sorption processes have also been applied for removal of similar organic contaminants from coking wastewaters (Zhang *et al*., 2010). This work explored the sorption of a simulated gasifierwastewater prepared by combining ten constituents selected from the groups, phenolics, heterocyclics and PAHs such that the overall COD was in the range commonly encountered for small scale gasifiers. In addition to activated carbon, rice husk char (RHC), a residue left after gasification of rice husk was also used as a sorbent. Sorption kinetics and sorption equilibrium were evaluated through batch studies.

2. Methodolgy

2.1 Chemicals

Naphthalene, phenanthrene, fluoranthene andpyrene were purchased from Sigma Aldrich (Mumbai, India). Quinoline,pyridine, benzene and phenol were procured from Merck Ltd.(Mumbai, India) and were of analytical grade.Commercial AC was procured from Merck (Mumbai, India) and RHC was collected from agasifier installation at Patna, Bihar.

2.2 Batch Sorption Experiments

The synthetic gasifier wastewater was formulated as suggested by Jeswani and Mukherji (2012) using ten components (mg/L): phenol (400); o-cresol (150); 1-naphthol (120); pyridine (200); quinolone (280); benzene (360); naphthalene (60); phenanthrene (0.5); fluoranthene (0.2) and pyrene (0.12). The total organics was measured in terms of COD and total phenolics were measured by the amino antipyrine method as per standard protocols. The kinetic and equilibrium studies were performed using the methods described by Mishra and Mukherji (2012) using a sorbent dose of 10 g/L. The set of bottles (crimp sealed with Teflon-lined septa) containing 50 mL of the simulated wastewater along with the desired sorbent was tumbled in a bottle rotator operated at 50 rpm. Bottles without sorbent were kept as controls. All studies were conducted at room temperature (30^0C $\pm 3^0$C). The samples were filtered before analysis of residual COD and phenolics in the aqueous phase at various time points. The kinetic studies were conducted over 12 hours and kinetic study data was analyzed using various models, such as the pseudo-first order model, pseudo-second order model and intraparticle diffusion model.The equation for these models expressing the mass of organics/phenolics adsorbed per unit mass of sorbent (q_t) as a function of time 't'and their linearized formsare described in Table 1.

Table 1: Kinetic models applied for fitting data for sorption of simulated gasifier wastewater on AC and RHC.

	Pseudo first order model	**Pseudo second order model**	**Intraparticle diffusion model**
Model Equation	$dq_t/dt = k_1(q_e - q_t)$	$dq_t/dt = k_2(q_e - q_t)^2$	$q_t = k_3 t^{0.5}$
Linearized form	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$1/(q_e - q_t) = 1/q_e + k_2 t$	$q_t = k_3 t^{0.5} + C$

The equilibrium study was set-up similarly using various dilutions of the synthetic wastewater and a constant dose of sorbent. Sampling was done after rotating the bottles for 12 hrs so as to allow equilibrium to be established. The amount of organics and phenolicssorbed per unit mass of sorbent at equilibrium (q_e) was calculated as suggested by Mishra and Mukherji (2012) (Equation 1). This approach accounts for loss due to volatilization and sorption on glassware.

$$q_e = (C_o\text{-}C_e/\hat{S})*V/m \qquad (1)$$

Where, $\hat{S}$= slope obtained from the graph of C_c versus C_o for the controls with no sorbents. Here C_o represents initial aqueous phase concentration of COD/phenolics;C_e represents final aqueous phase concentration after equilibrium is reached in the bottles containing sorbent and C_c represents the final aqueous phase concentration in the controls (without sorbent) after 12 hrs. Attempt was made to fit theequilibrium data using the Langmuir and Freundlichisotherm models.

3. Results and Discussion

The organic contaminants in synthetic wastewater were characterized in terms of the chemical oxygen demand (COD) (total organics) and phenolics.COD and phenolicsin the synthetic wastewater were determined as2343±53 and 772±10mg/L, respectively. Linear plot of $C_e$versus C_o for the controls with no sorbentsresulted in slope ($\hat{S}$) values of 0.98 for both COD and phenolics depicting negligible loss of organics and phenolics in the controls over the 12 hoursequilibriation period.Figure 1 shows the kinetic profile for sorption of organics (Figure 1a) and phenolics (Figure 1b) on AC and RHC. The kinetic profile shows that equilibrium can be attained within 12 hours. Moreover, for sorption of COD on AC, the decrease in concentration of organics in the aqueous phase was found to follow a biphasic profile with an initial phase of rapid decrease followed by a phase of slow decrease in concentration. Sorption of both total organics and phenolicsonRHCwas much lower compared to AC.

Fitting this data with the linearized form of the kinetic models indicated that organics removal on AC and RHC could be described by the pseudo-first order kinetic model and the R^2 values were found to range between 0.77-0.98. The pseudo-first order rate constant(k_1) for sorption on AC was0.22 (hr^{-1}) for COD and 0.25 (hr^{-1}) for phenolics. The correspondingrateconstant (k_1) for sorption on RHC was 0.15 (hr^{-1}) for COD and 0.18 (hr^{-1}) for phenolics. The linearized second order model also provided good fit (R^2=0.96) to sorption kinetic data for phenolics on AC with rate constant value of 0.008 (g mg^{-1} hr^{-1}). However, the pseudo-second order model could not provide good fit to sorption kinetic data for RHC. The intraparticle diffusion model also provided good fit to data for sorption on both these sorbents with R^2 ranging from 0.88-0.99. This model also indicated higher sorption rates for both COD and phenolics on AC compared to RHC.

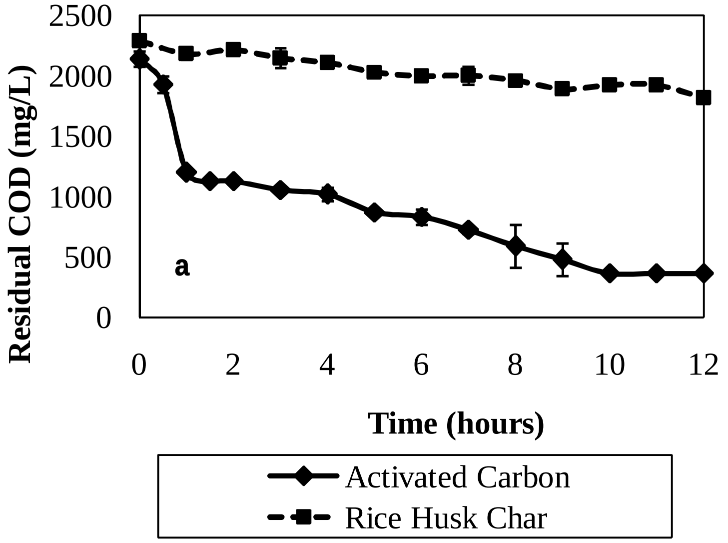
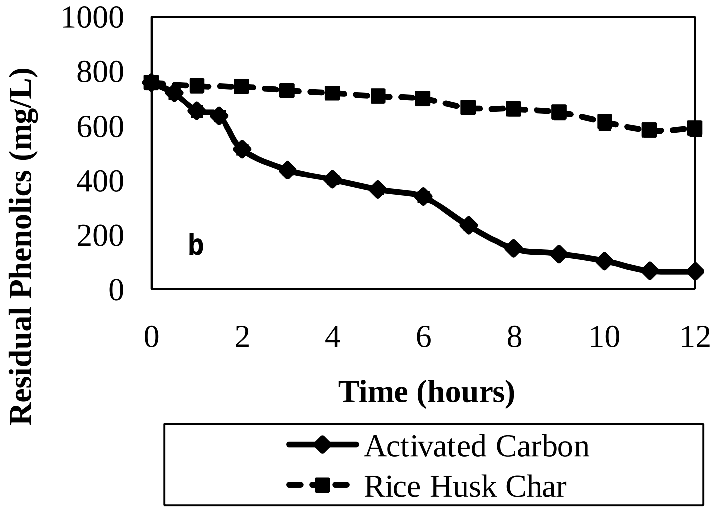


Figure 1: Kinetic profiles for (a) total organics (COD



(**b**) phenolics sorption on activated carbon and rice husk char

Sorption of organics on AC and RHC was found to be 192 and 75 mg-COD/g, respectively for the simulated gasifier wastewater at equilibrium (Figure 2a-b). Similarly, the sorption of phenolicsat equilibrium was observed to be 71 and 40 mg/g, respectively, for AC and RHC (Figure 2a-b). Attempt was made to fit the linearized form of Freundlich and Langmuir models to sorption isotherm data obtained for AC and RHC. The linearized Langmuir model did not provide a satisfactory fit to equilibrium sorption datafor total organics on AC and RHC. For sorption on AC negative intercept values were observed while for sorption on RHC the R^2 values were very low. In contrast, the linearized Freundlich isotherm ($q_e=K_FC_e^n$) provided good fits for organics and phenolics sorption on to AC and RHC with R^2 values in the range of 0.73-0.90.

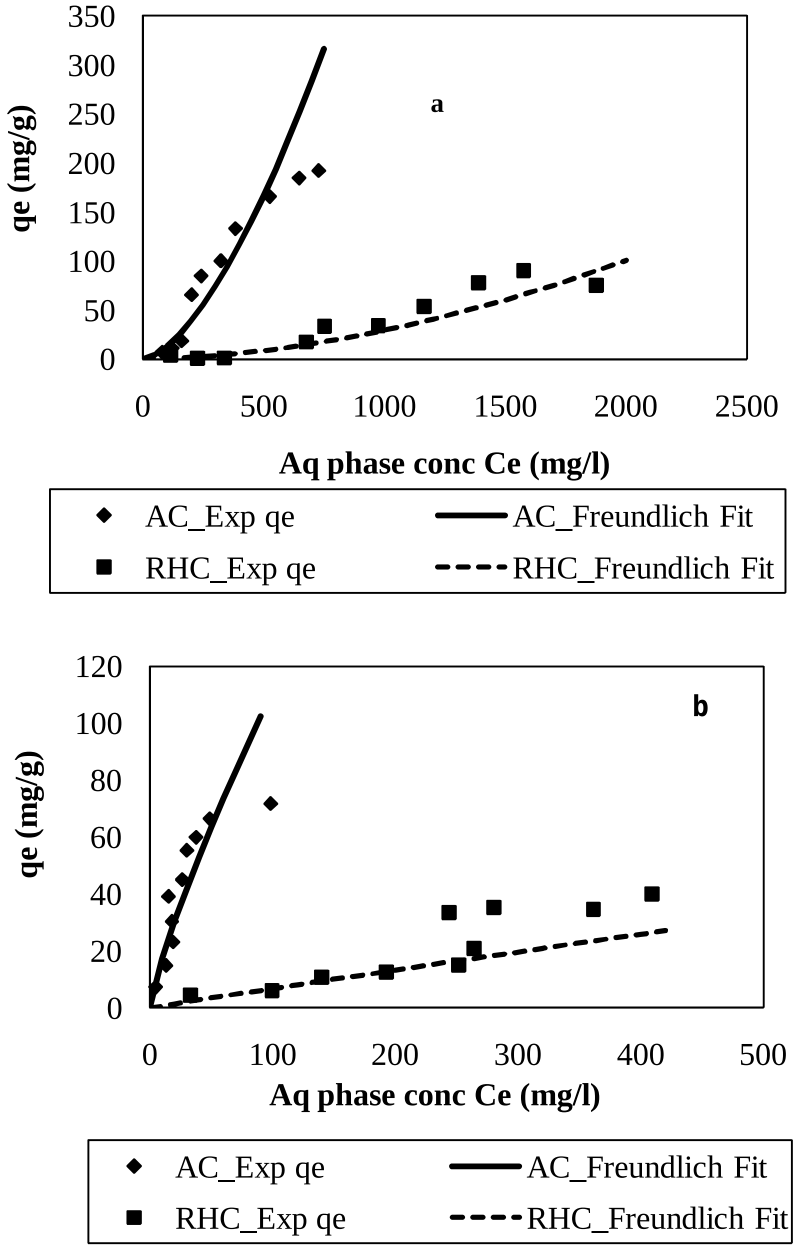


Figure 2: Sorption of (a) total organics (COD) and (b)phenolics on activated carbon and rice husk char at equilibrium and Freundlich model fit to data

The K_F value for sorption of organics from synthetic gasifier wastewater was found to be 0.009 and 0.00014 $(mg/g)(L/mg)^n$, respectively for AC and RHC. The corresponding 'n' values were 1.58 and 1.77 for AC and RHC indicating unfavourable sorption. Similarly, the K_F values for phenolics sorption were found to be 2.63 and 0.08 $(mg/g)(L/mg)^n$, respectively for AC and RHC. The corresponding 'n' value for AC was 0.81 while that for RHC was 0.97, indicating favourable isotherms. However, although the linearized Freundlich model appeared to fit the data well, the model fit to data appeared relatively poor on q_e versus C_e plots (Figure 2a-b), highlighting the inherent errors associated with obtaining model parameters through linear transformation. Similar results were observed for sorption of organics and phenols from wood based gasifier wastewater on powdered activated carbonwhere theFruendlich model was found to fit the equilibrium sorption data better than the Langmuir model (Mehta and Chavan 2009).

4. Conclusion

Sorption of synthetic gasifierwastewater on activated carbon and rice husk char were compared. The sorption of organics and phenolics on rice husk char was not found significant as compared to activated carbon. This implies that further chemical activation of rice husk char may be necessary for improving its sorption capacity for organic compounds. The kinetic study showed that total organicsand phenolicssorption on activated carbon and rice husk char were in agreement with the pseudo-first order kinetic model and intraparticle diffusion model. The sorption rates were higher for activated carbon compared to rice husk char. The Langmuir model could not be applied for sorption of organics on AC and RHC. Freundlich isotherm model could be used to depict sorption of organics and phenolics on AC and RHC. However, obtaining parameter estimates through linear transformations may lead to errors and may result in relatively poor model fit to experimental data.

5. Acknowledgement

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