

Treatment of phenolic wastewater using agricultural wastes as an adsorbent in a sequencing batch reactor

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Abstract The objective of this study is to investigate the potential of the activated rice husk to be used as an alternative adsorbent to powdered activated carbon (PAC) in the simultaneous adsorption and biodegradation processes under sequencing batch reactor (SBR) operation to treat synthetic wastewater containing phenol, *p*-methylphenol, *p*-ethylphenol and *p*-isopropylphenol. The rice husk (PRH) was activated by pyrolysis at 600°C for 5 hours in a nitrogen atmosphere. Using the Langmuir model, the limiting adsorption capacities of PRH for the phenols were found to vary from 0.015–0.05 of those of PAC. The SBR reactors with and without adsorbent addition were operated with fill, react, settle, draw and idle periods in the ratio of 4:6:1:0.75:0.25 for a cycle time of 12 hours. For phenolic wastewater containing, 1,200 mg/L phenol, 1,200 mg/L *p*-methylphenol, 800 mg/L *p*-ethylphenol and 650 mg/L *p*-isopropylphenol, it was found that the biodegradation process alone was unable to produce effluent of quality which would satisfy the discharge standards of COD \leq 100 mg/L and phenol concentration \leq 1 mg/L. The addition of PAC in the ratio of PAC/phenolic compound at 0.095 g/g for phenol, 0.119 g/g for *p*-methylphenol, 0.179 g/g for *p*-ethylphenol and 0.220 g/g for *p*-isopropylphenol, can improve the effluent quality to satisfy the discharge standards. Equivalent treatment performance was achieved with the use of PRH at dosages of 2–3 times higher than those of PAC for all the phenolic wastewater studied. The increased adsorption capacity of PRH shown in the treatment indicates bioregeneration of the adsorbed surface during the treatment process.

Keywords Agricultural wastes; sequencing batch reactor; treatment

Introduction

Phenol and alkyl phenols fall into the category of biodegradable organics and are known to have an inhibitory or toxic effect on the microorganism. Phenol was shown to be biologically treatable decades ago (Nayar and Sylvester, 1979; Brenner *et al.*, 1992; Yu and Gu, 1996). During biological treatment, phenol is degraded to its intermediates, some of which are resistant to further biodegradation. Powdered activated carbon (PAC) is added to the activated sludge system to remove the non-biodegradable residues through the adsorption process. The application of biomass and PAC in the same aeration basin for the respective removal of biodegradable and non-biodegradable compounds in wastewater is known as the PACT process. This kind of treatment, which utilizes simultaneous adsorption and biodegradation processes, was reported to be very effective in the treatment of toxic pollutants (Cecen, 1994; Lee *et al.*, 1989; Lim and Er, 2000; Lim *et al.*, 2002).

Large quantities of rice husk are generated in Malaysia as agricultural wastes and the proper disposal of them always poses a problem. There is some urgency in searching for the reutilization of the rice husk since the traditional way of burning the rice husk openly is no longer environmentally acceptable. In view of the relatively high cost of PAC, the potential of other materials such as rice husk, wood and peat, which may serve as a viable alternative to PAC, should be looked into. Chemical modification of rice husk is necessary to increase the adsorbability of the materials. Quarternized rice husk has been reported to sorb reactive dyes from synthetic solution and textile waste efficiently (Low and Lee, 1997). Other activation processes such as pyrolysis, acid or alkali activation, also appear to improve the adsorption efficiency of rice husk (Mmari *et al.*, 1998; Lim *et al.*, 2000). To

date, there has been no reported work on the utilization of activated rice husk as the adsorbent in the simultaneous adsorption and biodegradation processes under sequencing batch reactor (SBR) operation for the treatment of phenolic wastewater.

The objective of this research, therefore, is to evaluate the efficacy of pyrolyzed rice husk in comparison to PAC in the SBR system employing simultaneous adsorption and biodegradation processes for the treatment of wastewater containing phenol and its alkyl derivatives, namely *p*-methylphenol, *p*-ethylphenol and *p*-isopropylphenol.

Methods

Adsorption study

Raw rice husk was washed with tap water, then rinsed with distilled water and dried in an oven at a temperature of 103°C. The rice husk was blended, sieved into sizes <250 µm and then pyrolyzed at 600°C in a nitrogen atmosphere for 5 hours. The pyrolyzed rice husk (PRH) was cooled and kept in a desiccator prior to use. The deactivated biomass was prepared by autoclaving (at 121°C and 1.5 bar pressure for 25 minutes), 100 mL of the settled activated sludge obtained from the SBR treating a base mix with the composition listed in the following section.

The respective equilibrium adsorption isotherm of phenol, *p*-methylphenol, *p*-ethylphenol and *p*-isopropylphenol was determined. Exactly 0.02 g PAC was shaken with 25.0 mL phenolic solution with concentrations varying from 50 to 500 mg/L for a contact time of 5 hours. Predetermination of the equilibrium contact time for the adsorption of phenols on PAC was 4 hours. After shaking, the solution was immediately centrifuged and the supernatant analyzed for the residual phenolic concentration with λ_{\max} as follows: phenol (269 nm), *p*-methylphenol (276.6 nm), *p*-ethylphenol (274.4 nm) and *p*-isopropylphenol (275.2 nm) using an UV-VIS spectrophotometer (Hitachi Model U-2000) following the procedure described by Singer and Yen (1980).

The adsorption of the phenols on PRH and deactivated biomass were also studied. A weight of 0.7 g PRH and 15 mL of deactivated biomass were used. The agitation periods for both PRH and biomass were 12 hours (equilibrium contact time for the adsorption of phenols on PRH and biomass was 8 hours). The phenolic concentration range and analytical procedure were identical to those for PAC described above.

Treatment process with and without PAC and PRH

A total of eight identical reactors were built from plexiglass with the dimensions of 30 × 25 × 20 cm. They were identified according to the phenolic compound treated and adsorbent used. For instance, CP and RP denoted reactors treating phenol with PAC and PRH as adsorbents, respectively, whereas CM and RM were for *p*-methylphenol with PAC and PRH, respectively. Each reactor was operated at a cycle time of 12 hours with fill, react, settle, draw and idle periods per cycle in the ratio of 4:6:1:0.75:0.25. Aeration was applied to the system during the fill and react periods. This operating scheme was adopted based on good settleability of the sludge with the sludge volume index (SVI), consistently less than 100 mL/g. A fill period of 4 hours was also adopted to avoid sludge foaming due to shock loading of the activated sludge at high concentration of phenolic compounds. The total working volume of the reactor was 10 L. In each cycle, 7 L of feed solution was introduced during the fill period and then the same amount of treated effluent was drawn after settling for one hour.

The activated sludge seed was obtained from a local municipal sewage treatment plant and acclimatized to a synthetic waste of peptone, sucrose, nutrients and buffer solution in the following composition (concentrations in mg/L): bacto-peptone (188), sucrose (563), NH₄Cl (344), MgSO₄ (49), FeCl₃ (11.3), K₂HPO₄ (120), KH₂PO₄ (160) and NaHCO₃

(100) giving an equivalent COD of 800 mg/L. During four weeks of acclimatization, the peptone and sucrose were gradually replaced by the respective phenolic compound totally as the substrate. The concentration of phenolic compound used was then gradually increased to 1,200 mg/L for phenol and *p*-methylphenol, 800 mg/L for *p*-ethylphenol and 650 mg/L for *p*-isopropylphenol. Once the reactors had achieved the steady state characterized by a fairly constant effluent COD (less than 10% variation), the profiles of the concentrations of COD and phenolic compounds during the fill and react periods were determined.

Adsorbents, namely PAC and PRH, were then introduced into the respective reactors in increasing amounts. The dosage of adsorbent was calculated based on the ratio between the amount of adsorbent to the amount of phenolic compound (g/g) introduced into the reactor per cycle. For PAC, the dosages were: phenol, 0.024–0.095 g/g; *p*-methylphenol, 0.024–0.119 g/g; *p*-ethylphenol, 0.036–0.179 g/g and *p*-isopropylphenol, 0.044–0.220 g/g. For PRH, the corresponding dosage ranges were: 0.024–0.179, 0.024–0.238, 0.036–0.357 and 0.044–0.660 g/g. During this period, the concentrations of effluent COD and phenolic compounds of all the reactors were monitored to gauge the performance of the reactors. In addition, the COD and phenolic concentration profiles during the fill and react periods were again determined. The COD was analyzed according to the *Standard Methods for the Examination of Water and Wastewater* (1985) whilst the concentrations of phenolic compounds were measured spectrophotometrically as described above. The determination of mixed liquor adsorbent concentration (MLCSS) and that of biomass concentration (MLBSS) followed the method described by Arbuckle and Griggs (1982).

Results and discussion

Adsorption study

The data were fitted to the Langmuir adsorption isotherm expressed as:

$$\frac{C_e}{Q} = \frac{1}{bQ^0} + \frac{C_e}{Q^0} \quad (1)$$

where Q is the amount of adsorbate adsorbed per unit mass of adsorbent, C_e is the equilibrium adsorbate concentration, Q^0 is the limiting adsorption capacity and b is the Langmuir parameter related to the energy of adsorption. The Langmuir parameters, Q^0 and b , at the natural pH of the four phenolic compounds, were obtained by fitting the data to Eq. (1) ($R^2 > 0.9$) and are listed in Table 1. The values of the limiting adsorption capacities (Table 1) indicate that the adsorption of phenolic compounds by PAC was very much higher compared to PRH and biomass adsorption. The limiting adsorption capacities of PRH for the phenols were found to vary from 0.015 to 0.05 of those of PAC. For the biomass, the Q^0 values were very much smaller compared to those of PAC or even PRH.

It is therefore evident that the role of biomass in the adsorption of the phenolic compounds can be neglected. Table 1 also shows that the adsorption of phenol on PAC was the lowest compared to the other alkylphenols. Thus, the data indicate that the longer the alkyl

Table 1 Langmuir parameters

Adsorbate	Q^0 (mg/g)			b (L/mg)		
	PAC	PRH	Biomass	PAC	PRH	Biomass
Phenol	233	12	1.2	0.031	0.011	0.012
<i>p</i> -methylphenol	286	8.1	1.1	0.046	0.038	0.017
<i>p</i> -ethylphenol	303	8.5	1.1	0.097	0.009	0.015
<i>p</i> -isopropylphenol	345	5.1	1.1	0.110	0.009	0.016

chain, the higher the Q^0 value with *p*-isopropylphenol having the highest Q^0 value. The parameter b , which indicates the energy of adsorption, also increases with chain length. The results are consistent with those reported by Singer and Yen (1980). This can be explained by the fact that the solubility of the alkylphenols decreases when the hydrophobic alkyl chain becomes longer and less polar and thus, they tend to be more readily adsorbed on the PAC. The reverse trend was observed for the adsorption of alkylphenols on PRH (Table 1).

Treatment process with and without PAC and PRH

Figures 1a to 1d and 2a to 2d depict the observations for COD and phenolic concentrations in the effluents of various reactors with increasing PAC and PRH dosages, respectively. Without the adsorbents, it is observed that the effluent COD and phenolic concentrations were in the region of 200–250 mg/L and 2–6 mg/L, respectively. Increasing dosages of PAC and PRH, respectively, were able to reduce the effluent COD and phenolic concentrations progressively. At the dosages of 0.096 g PAC/g phenol in reactor CP or 0.179 g PRH/g phenol in reactor RP, the effluent COD and phenol concentrations were reduced to below 100 and 1.0 mg/L, respectively (Figures 1a and 2a). In reactors CM and RM, the

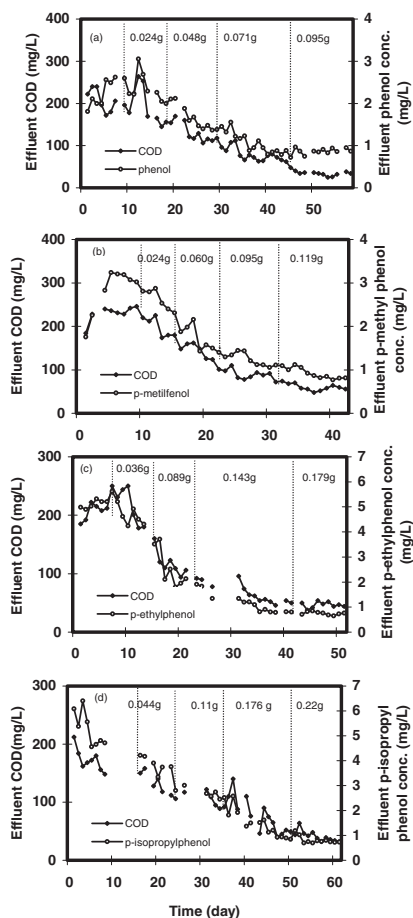


Figure 1 The effluent COD and phenolic concentrations of reactors: (a) CP; (b) CM; (c) CE; and (d) CI, with increasing PAC dosages (g/g phenol or alkylphenol)

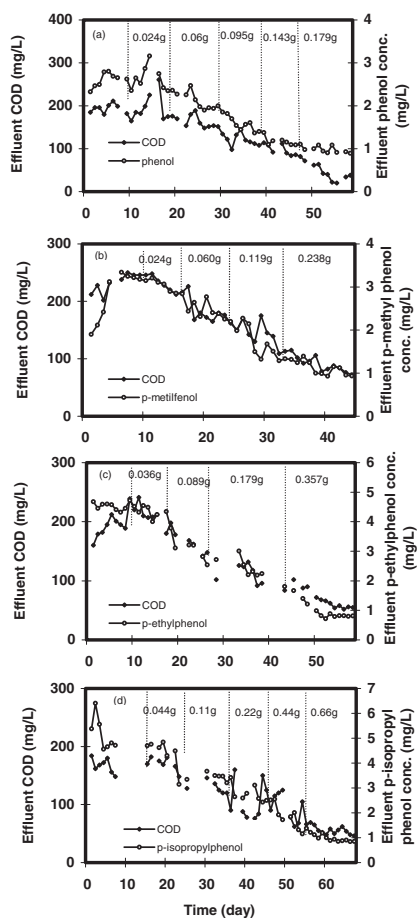


Figure 2 The effluent COD and phenolic concentrations of reactors: (a) RP; (b) RM; (c) RE; and (d) RI with increasing PRH dosages (g/g phenol or alkylphenol)

effluent COD and *p*-methylphenol concentrations were reduced to below 100 mg/L and 1.0 mg/L at dosages of 0.119 g PAC and 0.238 g PRH/g *p*-methylphenol, respectively, (Figures 1b and 2b). Figures 1c and 2c show the effect of increasing PAC and PRH dosages on the effluent COD and *p*-ethylphenol concentrations in reactors CE and RE, respectively. At 0.179 g PAC or 0.357 g PRH/g *p*-ethylphenol, the effluent COD and alkylphenol concentrations in both reactors were reduced to below 100 and 1.0 mg/L. The progressive decrease in the effluent COD and *p*-isopropylphenol concentrations of reactors CI and RI on increasing adsorbent dosages is shown in Figures 1d and 2d, respectively. A dosage of 0.220 g PAC or 0.660 g PRH/g *p*-isopropylphenol was required to bring the effluent COD and *p*-isopropylphenol concentrations in the respective reactor to below 100 and 1.0 mg/L, respectively.

Figures 3a and 4a show the COD and phenol concentration profiles, respectively, in the mixed liquor of reactors CP and RP at various MLCSS (PAC or PRH) concentrations during the fill and react periods of a typical cycle. It was observed that the react period can

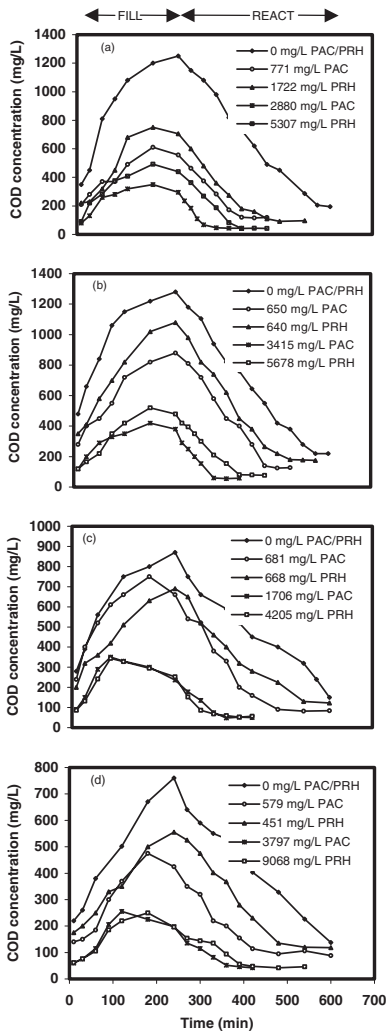


Figure 3 The COD concentration profiles in the mixed liquors of reactors: (a) CP and RP; (b) CM and RM; (c) CE and RE; and (d) CI and RI, with increasing accumulated PAC and PRH concentrations

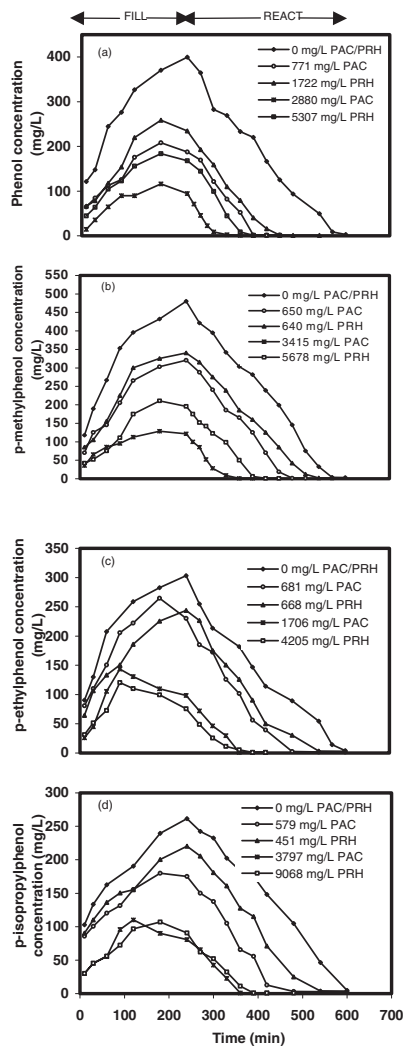


Figure 4 The phenolic concentration profiles in the mixed liquors of reactors: (a) CP and RP; (b) CM and RM; (c) CE and RE; and (d) CI and RI, with increasing accumulated PAC and PRH concentrations

be shortened from about 600 minutes without PAC addition to about 300 minutes when the MLCSS (PAC) concentration in reactor CP had reached 2,880 mg/L. In the case of PRH, the react period was shortened to 390 minutes only even with the higher MLCSS (PRH) concentration of 5,300 mg/L accumulated in reactor RP. Thus, equivalent treatment performance was achieved with the MLCSS (PRH) concentration about twice that of the MLCSS (PAC) concentration. Figures 3b and 4b show the effect on the COD and *p*-methylphenol concentration profiles, respectively, in the mixed liquor of reactors CM and RM during the fill and react periods before and after the addition of adsorbents resulting in increasing MLCSS concentrations in the respective reactor. It was found that the react period can be shortened from about 600 minutes without adsorbents to about 390 minutes when around 2,400 mg/L of PAC and 5,600 mg/L of PRH had accumulated in reactors CM and RM, respectively. Thus, similar to the case of phenol, about twice the amount of PAC was required to attain equivalent performance if PRH was used as the adsorbent.

The relative efficacy of both adsorbents can also be evaluated by observing the effect of increasing MLCSS (PAC or PRH) concentrations on the COD and *p*-ethylphenol concentration profiles in the mixed liquor of reactors CE and RE during the fill and react periods (Figures 3c and 4c). It was found that the react period can be shortened from 600 minutes without the addition of adsorbents to 360 minutes when about 1,700 mg/L of PAC or 4,200 mg/L of PRH was accumulated in the respective reactor. Apparently, the amount of PRH required was about 2.5 times of that of PAC in this case. Based on the profiles of COD and *p*-isopropylphenol concentrations during the fill and react periods of a typical cycle with and without the addition of adsorbents, the react period can be shortened from about 600 minutes without adsorbent addition to about 390 minutes in the presence of about 2,800 mg/L PAC in reactor CI or about 9,000 mg/L PRH in reactor RI (Figures 3d and 4d). The quantity of PRH required was approximately three times that of PAC to achieve the same treatment performance.

Role of bioregeneration in the treatment process

The important role of bioregeneration process in renewing the adsorbent surface for further adsorption of organics during simultaneous adsorption and biodegradation processes has been well recognized (Sublette *et al.*, 1982; Schultz and Keinath, 1984; Jonge *et al.*, 1996). The extent of bioregeneration varied considerably depending on the type of adsorbent used and adsorbate involved. Jonge *et al.* (1996) have further proposed that desorption of organics occurs prior to biodegradation in the bulk solution. Desorption of biodegradable compounds will lead to a renewal of the surface of the adsorbent and thus increase the adsorptive capacity of the adsorbent. A possible explanation for the observed increase in the adsorptive capacity of PRH relative to that of PAC during the simultaneous treatment processes is that desorption of phenolic compounds from the PRH proceeded at a faster rate than from the PAC. This offsets the relatively much lower adsorptive capacity of PRH for phenolic compounds when compared to PAC as estimated from the Langmuir model.

Conclusions

Activated rice husk (PRH) can be used as an alternative adsorbent to PAC in the simultaneous adsorption and biodegradation treatment processes for the removal of phenol and alkylphenols in the wastewater. The estimated dosage required for PRH is about 2–3 times that of PAC to achieve equivalent performance. Since the limiting adsorption capacities of PRH for the phenols as estimated from the Langmuir model were only 0.015–0.05 of those of PAC, the observed increase of adsorption capacity of PRH indicates bioregeneration of the adsorbed surface during the simultaneous adsorption and biodegradation of alkylphenols. The addition of adsorbent in the SBR process can reduce the react period

considerably, and this has the implication of considerable energy savings due to shortened aeration time and an increased quantity of wastewater that can be treated.

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