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Activated rice husk-based adsorbents for chlorophenol removal and their bioregeneration

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ABSTRACT

Studies on the development of alternative adsorbent using rice husk have been extensively reported. However, relatively little has been reported on the comparative adsorptive removal of phenolic compounds using rice husk activated with different methods as well as their bioregeneration potential and reusability. This study aimed to investigate the adsorption capacities of rice husk activated with nitric acid (ARH), ethylenediamine (MRH), and potassium hydroxide (KRH), respectively, for 4-chlorophenol (4-CP) and 2,4-chlorophenol (2,4-DCP) in comparison to powdered activated carbon (PAC) and the bioregeneration efficiencies and reusability of chlorophenol-loaded activated rice husks. For both cases using 4-CP and 2,4-DCP as adsorbates, the adsorption capacities were found in the order of KRH > PAC > ARH > MRH. Despite the much lower abiotic desorption efficiencies, the bioregeneration efficiencies were found comparable for all the adsorbents (>80% for the first cycle except for 2,4-DCP-loaded KRH). The total capacity losses for all the bioregenerated adsorbents were observed to increase with increasing number of cycles of use. In terms of the efficacy, KRH showed the highest accumulated amount of 4-CP and 2,4-DCP removed followed by PAC, ARH, and MRH. Amongst the adsorbents, KRH was found to be the most efficient adsorbent to remove 4-CP and 2,4-DCP, respectively, based on the accumulated amount of adsorbate after successive bioregeneration.

Keywords: Activated rice husk; Chlorophenols; Adsorption; Bioregeneration

1. Introduction

Chlorophenols are prevalent in wastewaters from pesticide, paint, solvent, pharmaceutics, wood, paper and pulp industries as well as water disinfecting process [1]. Discharge of these chlorophenol-containing wastewater into receiving waters poses serious risk to aquatic organisms and human beings besides imparting unpleasant odor and taste. Therefore, it is essential to remove these compounds from wastewater before discharge. Adsorption is a process widely used in removing these xenobiotic pollutants from wastewater before discharge due to its simplicity and high

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efficiency. The important mechanisms that have been proposed to interpret the adsorption behavior between adsorbent and phenolic compounds are mainly electron donor–acceptor complex and π–π dispersion interactions, respectively [2]. The electron donor–acceptor complex mechanism assumes that the aromatic rings of the adsorbate act as the electron acceptors and the basic sites on the carbon surface serve as the donors. In the other mechanism, the adsorption involves the π–π dispersion interactions derived from the interactions between the π electrons in the aromatic rings of the phenols and in the graphitic planes of adsorbent. The presence of electron-withdrawing groups, such as nitro and chloro, favors the formation of electron donor–acceptor complexes [3] and enhances the π–π interactions [4]. During adsorption, the pollutants are retained and concentrated on the surface of an adsorbent. The adsorption capacity of an adsorbent depends on three major factors: (i) the physical nature of the adsorbent, (ii) the nature of the adsorbate, and (iii) the solution conditions [5].

Commercial activated carbon is the preferred adsorbent due to its microporous structure. However, attempts have been made to use agricultural byproducts as the alternative adsorbents [6]. Rice husk is among those which were chosen as the precursor because it is an abundant agricultural byproduct from rice milling industries. Development of rice husk-based adsorbents activated with different methods has been widely reported [7–10], but there are very few studies on the removal of phenolic compounds using the alkali-activated rice husks. Although the development of an adsorbent with high adsorption capacity is the main interest for most researchers, the regeneration potential of the adsorbent should also be taken into account. The service life of the adsorbent can be extended through regeneration of the spent adsorbent. In this respect, efforts have been made by many researchers using chemical [11,12] and physical [13,14] regeneration methods. Among the various methods, regeneration through microbial action (bioregeneration) would be a better alternative due to its environmentally friendly and economical operation as the desorbed organic pollutants could be mineralized without additional treatment.

To date, most of the bioregeneration studies were found to focus on commercially available activated carbon [15–19] and relatively little had been reported on the bioregeneration of adsorbents derived from agricultural waste, especially on the effect of different activation methods on the bioregeneration efficiency and the reusability of the bioregenerated adsorbents. By right, the factors affecting both the adsorption capacity and regeneration should be considered in order to develop successfully an alternative adsorbent with high adsorption capacity and bioregeneration potential.

In light of the above observation, the objectives of this study are: (i) to investigate the effects of different activation methods on the adsorption capacities of activated rice husk for 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP), (ii) to determine the one-cycle bioregeneration efficiency of chlorophenol-loaded activated rice husks, and (iii) to evaluate the reusability of bioregenerated-activated rice husks.

2. Materials and methods

As chlorophenols are toxic compounds, the adopted precautionary measures involved the use of respiratory protective device and gloves when handling these compounds and their disposal according to official regulations.

2.1. Preparation and characterization of adsorbents

The raw rice husk obtained from a rice mill located in Penang, Malaysia was washed with tap water and rinsed with distilled water to remove impurities. After drying in an oven at 105˚C until constant weight, the raw rice husk was ground and sieved to size <250 μm. Three types of activated rice husk, namely ARH, MRH, and KRH, were prepared by activating the sieved raw rice husk with different activation methods. The ARH was prepared following the activation method described by Akhtar et al. [7]. Briefly, a total of 200 g sieved rice husk was stirred with 0.1 M nitric acid for 1 h followed by soaking in methanol for 4 h. The product was then washed continuously with distilled water until the washing solution was neutral and subsequently subjected to thermal activation process by carbonizing at 300˚C for 1 h. For MRH, 100 g of raw rice husk was stirred with 121.41 g of ethylenediamine in a water bath at 80˚C for 2 h. Subsequently, the rice husk was washed with distilled water, dried at 70˚C, and finally carbonized at 300˚C for 1 h. The third activated rice husk, KRH, was prepared by thermal and chemical activation with KOH. Firstly, raw rice husk was carbonized at 300˚C for 1 d. Subsequently, 50 g of carbonized rice husk was impregnated with 50% (w/v) of potassium hydroxide at room temperature for 1 d, dried at 105˚C, and subjected to pyrolysis under N_2 atmosphere at 800˚C for 1 h. The product was then washed with distilled water until the washing solution was neutral and dried at 105˚C. For comparison, commercial powdered activated carbon (PAC), MALBON S4 (steam-activated wood-based carbon), was used. The PAC was dried at 105˚C for 24 h and cooled in desiccator prior to use.

The adsorbents were analyzed for functional groups using FTIR spectrophotometer (FTIR-2000, Perkin Elmer). The points of zero charge (pH_{PZC}) of the adsorbents were determined by an immersion technique [20]. The surface morphology was studied using SEM (Leo Supra 50VP), whereas the specific surface area, pore volume, and pore diameter of the adsorbents were characterized with an automatic sorption analyzer (Quantachrome Nova 2200e) at 77 K using N_2 as the adsorbate.

2.2. Equilibrium adsorption and abiotic desorption studies

Equilibrium adsorption studies were carried out to determine the adsorption capacities of ARH, MRH, KRH, and PAC for 4-CP and 2,4-DCP, respectively. Since the natural pH values of 4-CP and 2,4-DCP were found to be 5.9 ± 0.1 and 4.9 ± 0.1, respectively, which were far less than the pK_a values of 9.37 and 7.90 for the respective compound, this implies that the chlorophenols would exist in non-ionic forms. As such, there would be negligible pH effect on the adsorption capacities. Exactly 0.4 g of ARH was shaken with 100 mL of 4-CP or 2,4-DCP with concentrations varying from 100 to 500 mg/L without pH adjustment at 250 rpm for 5 h. The shaking period was sufficient for the attainment of equilibrium based on the preliminary contact time study. At the end of the shaking period, the samples were filtered and the filtrates were analyzed for equilibrium chlorophenol concentrations using 4-aminoantipyrine method [21] at λ_{max} of 504 nm for 4-CP and 508 nm for 2,4-DCP. The equilibrium adsorption studies were repeated for 0.4 g MRH, 0.04 g KRH, and 0.08 g PAC with shaking periods of 6, 3, and 4 h, respectively.

Batch desorption experiments were carried out to investigate the abiotic desorption of chlorophenol-loaded ARH, KRH, MRH, and PAC at various dosages (under non-excess and excess conditions). Desorption isotherms were constructed according to batch displacement technique [22]. The loaded adsorbents from the above-mentioned equilibrium adsorption studies were resuspended into 100 mL distilled water and shaken for 24 h to reach desorption equilibrium. The sample solutions were then filtered and the amount of desorbed 4-CP or 2,4-DCP was determined. The abiotic desorption efficiencies for all the adsorbents were determined at different initial chlorophenol concentrations (C_L) using Eq. (1).

$$\text{Desorption efficiency } (\%) = \frac{Q_d}{Q_a} \times 100 \qquad (1)$$

where Q_d and Q_a are the amounts of desorbed and adsorbed adsorbates, respectively, in mg/g.

2.3. Bioregeneration studies

2.3.1. Cultivation of chlorophenol-acclimated biomasses

4-Chlorophenol- and 2,4-DCP-acclimated biomasses, respectively, were cultivated by operating two identical 5-L laboratory-scale sequencing batch reactors (SBRs) with FILL, REACT, SETTLE, DRAW, and IDLE periods in the time ratio of 2:8:1:0.75:0.25 for a cycle time of 12 h. The seed was obtained from a local municipal sewage treatment plant and acclimated to the base mix containing bacto-peptone, sucrose, and nutrients with the following composition (concentration in mg/L): $(NH_4)_2SO_4$ (212), KH_2PO_4 (32), K_2HPO_4 (180), $MgSO_4$ (49), $NaHCO_3$ (354), $FeCl_3{\cdot}6H_2O$ (18.8) and $CaCl_2$ (40) for 3 months. The biomass was then gradually acclimated to 4-CP or 2,4-DCP by replacing bacto-peptone and sucrose with increasing concentration of the respective chlorophenol as the sole carbon sources (20–400 mg/L 4-CP and 10–200 mg/L 2,4-DCP). The chlorophenol-acclimated biomass was used in the subsequent bioregeneration studies once the system had attained the steady state as indicated by fairly constant concentrations of mixed liquor suspended solids in the reactor and chlorophenol as well as the effluent COD concentration.

2.3.2. Determination of bioregeneration efficiency

Batch bioregeneration studies were carried out using sequential adsorption and biodegradation approach [17]. The adsorbents were pre-loaded with the 4-CP and 2,4-DCP, respectively, and then allowed to come into contact with acclimated biomass to achieve bioregeneration. Based on the maximum adsorption capacities determined from the equilibrium adsorption studies, 400 mg/L of 4-CP and 200 mg/L of 2,4-DCP were chosen, respectively, and used for the adsorptive loading process to produce saturated adsorbents at the respective dosages. Initially, 1.3 g/L of fresh ARH was stirred with 400 mg/L of 4-CP for 5 h until the equilibrium was attained. The saturated ARH was then filtered through a 0.45 μm membrane filter. The concentration of residual 4-CP in the filtrate was measured using 4-aminoantipyrine method [21] to determine the amount of 4-CP adsorbed onto ARH ($Q_{initial}$, mg/g). The 4-CP-saturated ARH was then resuspended in a 300-mL amber bottle containing the nutrient solution with the same composition as the base mix mentioned previously and 200 mg/L of 4-CP-acclimated biomass. The content was then stirred for 48 h. Subsequently, the sample solution was filtered and the bioregenerated ARH was resuspended in water acidified to pH 2 with 1 M hydrochloric acid to deactivate the bioactivity and stirred for 12 h. The amount of bioregenerated ARH was then quantified by direct measurement of residual amount of 4-CP adsorbed on ARH following the reloading method as described in Oh et al. [18]. In this study, the bioregenerated ARH was reloaded to saturation (Q_{sat}, mg/g) with 400 mg/L of 4-CP at pH 2. In all the cases, non-excess dosages of adsorbents were used, in which case $Q_{\mathrm{sat}} = Q_{\mathrm{initial}}$. After reloading, the mixture was filtered through a 0.45 μm membrane filter and the concentration of 4-CP in the filtrate was analyzed. The amount of 4-CP adsorbed during reloading was determined as the amount of bioregenerated ARH (Q_{reg}, mg/g). The efficiency of one-cycle bioregeneration was determined using Eq. (2):

$$\text{Bioregeneration efficiency } (\%) = \frac{Q_{\mathrm{reg}}}{Q_{\mathrm{initial}}} \times 100 \qquad (2)$$

where Q_{initial} and Q_{reg} are the amount of initial adsorbed substrate and the amount of desorbed substrate after bioregeneration, in mg/g, respectively.

The experiment to determine the bioregeneration efficiency was repeated, respectively, for MRH (1.7 g/L), KRH (0.2 g/L), and PAC (0.3 g/L) loaded with 4-CP and for ARH (0.7 g/L), MRH (1 g/L), KRH (0.13 g/L), and PAC (0.2 g/L) loaded with 2,4-DCP.

2.3.3. *Evaluation of reusability of bioregenerated adsorbents*

The reusability of the bioregenerated adsorbents was investigated by conducting multi-cycles of bioregeneration-loading processes. The first cycle of bioregeneration was carried out as described in the previous section. The reloaded adsorbent from the first cycle of bioregeneration was used for the second cycle of bioregeneration. The bioregenerated capacity from second cycle was determined using the reloading method as described above. The loading-bioregeneration cycles were repeated five times for both 4-CP- and 2,4-DCP-loaded adsorbents. Total capacity loss after each cycle of bioregeneration was determined using Eq. (3)

$$\text{Total capacity loss } (\%) = \frac{Q_{\mathrm{i}}}{Q_{\mathrm{initial}}} \times 100 \qquad (3)$$

where Q_{i} is the amount of undesorbed chlorophenol in the ith cycle, in mg/g.

3. Results and discussion

3.1. *Characterization of activated rice husks and PAC*

Fig. 1 shows the FTIR spectra for raw rice husk (RH), activated rice husks of ARH, MRH and KRH, and PAC. The bands at approximately 3,420 cm^{-1} in all the spectra were related to the free hydroxyl groups (–OH) or adsorbed moisture. The bands near 2,330 cm^{-1} corresponded to the vibration in alkanes and alkyl groups. The bands near 1,700 cm^{-1} were attributed to the carbonyl groups (C=O) stretching vibration of ketones, aldehydes, lactones, or carboxyl groups. The peaks near 1,380 cm^{-1} were assigned to C–H stretching in alkanes/alkyl groups. The peaks in the spectra of KRH and PAC at around 1,120 cm^{-1} were attributed to the C–O–C stretching. The peaks in the spectrum of RH at around 1,100, 800 and 470 cm^{-1} corresponded to the siloxane groups (–Si–O–Si–OH) and these peaks were also observed in the spectra of ARH and MRH. However, the peaks were not detected in the spectrum of KRH indicating the removal of silica by KOH. The peak around 1,600 cm^{-1} detected for RH, ARH, and MRH was attributed to the carbonyl groups (–C=O). The peak near 2,930 cm^{-1} for RH was indicative of the C–H vibrations and was absent in the spectra of all the activated rice husks.

Fig. 2(a)–(f) shows the SEM images for RH and activated rice husks. It was observed that fibers interspaced within matrix of lignin and cellulose at the outer epidermis of the RH (Fig. 2(a) and (b)). This corrugated structure was retained for ARH and MRH by the strong layer of silica despite the activation process. For inner epidermis and cross-sections, it was observed that the strong layer of fibers led to the shrinkage of ARH and MRH (Fig. 2(c) and (d), respectively) in the transverse direction with the formation of pores appearing as channels where the cellulosic content was removed during the activation process. For KRH, the creation of pores was observed at both the outer and inner epidermis. The SEM images of KRH were found to be similar to the study of Tseng and Tseng [23]. They showed that the surface of KOH-activated corncob had an irregular cottony feature if the KOH/char ratio was less than 1. The surface of KRH also showed irregular cottony feature on the surface of holes. From Fig. 2(e), contracted, twisted, thin, and deformed walls of honeycomb holes were clearly found. The soaking of KOH promoted the etching during the activation process, which created micropores within mesopores (Fig. 2(f)).

From the nitrogen adsorption and desorption isotherms at 77 K for activated rice husks and PAC (data not shown), it was observed that all the adsorbents

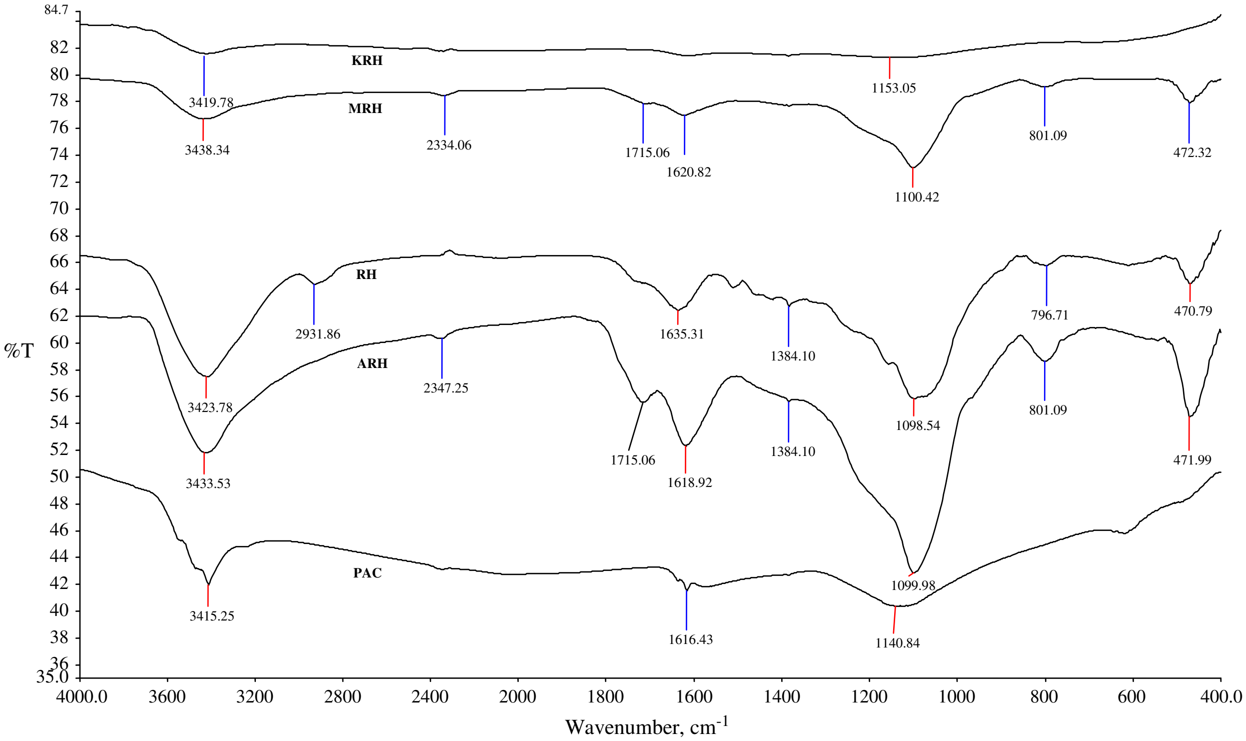

Fig. 1. FTIR spectra for raw rice husk (RH), activated rice husks (ARH, MRH, and KRH) and PAC.

exhibiting type IV adsorption isotherm showing microporous and mesoporous characteristics [24]. The isotherms of RH, activated rice husks, and PAC have been interpreted quantitatively and are presented in Table 1. In comparison to that of RH, the BET surface areas of the ARH, MRH, and KRH were observed to increase tremendously to different extent depending on the activation method. Amongst the activated rice husks, KRH was observed to have the highest surface area of 1,465 m^2/g, approximately 1.7 times higher than that of commercial PAC. From the experimental results of pH_{pzc} determination, the pH_{pzc} values of ARH, MRH, KRH, and PAC were found to be 2.90, 3.28, 7.01, and 7.05, respectively, in which ARH and MRH were of acidic nature while KRH and PAC were of basic nature. The surface of the adsorbent will be negatively charged if the pH solution ranged above the respective value of pH_{pzc}.

3.2. *Adsorption and abiotic desorption studies*

Table 2 shows the Langmuir and Freundlich isotherms parameters for the adsorption of 4-CP and 2,4-DCP, respectively, onto different adsorbents at 298 K. The trend of monolayer maximum adsorption capacity (q_m) was found to agree with the trend of BET surface area results, which was KRH > PAC > ARH > MRH. Higher adsorption capacities observed for 2,4-DCP compared to those for 4-CP for all the studied adsorbents were due to the additional electron-withdrawing chloro group in the 2,4-DCP aromatic ring which favors the formation of electron donor–acceptor complex, one of the important adsorption mechanism proposed by Moreno-Castilla [2]. For both cases of using 4-CP and 2,4-DCP as the adsorbates, PAC showed the highest value of Langmuir constant, K_L, indicating its greatest affinity of binding site for the adsorbates, followed by KRH, ARH, and MRH. The strong interaction between PAC and the adsorbates was also observed from the greatest values of n obtained from the Freundlich isotherm equation.

It was documented that bioregeneration was dependent on the reversibility of adsorption, which varies with the types of adsorbent and adsorbate [15,25–28]. Desorption was also found to be the rate-determining step for bioregeneration process [29]. Therefore, abiotic desorption experiments were conducted in this study to investigate the reversibility of adsorption and thus the bioregeneration potential of the adsorbents used. The abiotic desorption efficiencies for all the adsorbents were determined at different initial chlorophenol concentrations (C_L) using Eq. (1) and the results are shown in Table 3. Based on the Langmuir maximum monolayer adsorption capacities,

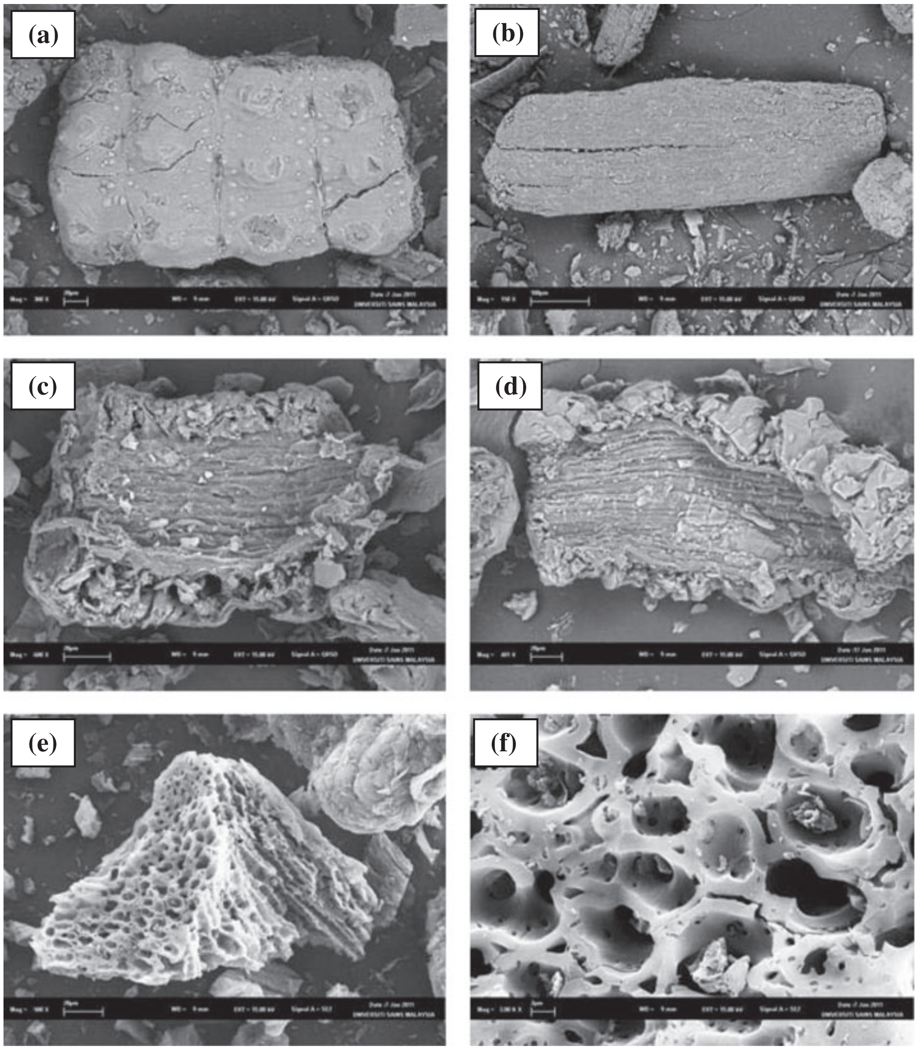

Fig. 2. SEM images (magnification) of (a) RH-concave surface area (300×), (b) RH-concave surface area (150×), (c) ARH-concave surface area (600×), (d) MRH-concave surface area (400×), (e) KRH surface area (500×), and (f) KRH surface area (3,000×).

the abiotic desorption of the adsorbents was carried out under both non-excess and excess adsorbent conditions depending on the initial loading concentration. In an excess adsorbent condition (low C_L value), there were many active sites available for adsorption during which the adsorbate would preferably be adsorbed into micropores [29]. When C_L increased, some of the mesopores would also be occupied. It is predicted that the potential of chlorophenol to be desorbed from mesopores is greater than from micropores due to lower energy of adsorption at mesopores [28]. Several observations could be made: (i) the results of the desorption efficiencies as shown in Table 3 indicate that there was higher irreversibility in the adsorption of 2,4-DCP than 4-CP, which could be attributed to the lower polarity and solubility of 2,4-DCP, (ii) the trend of abiotic desorption efficiencies for both 4-CP and 2,4-DCP was in the order of MRH > ARH > KRH > PAC, which agree with the trend of Langmuir constants as shown in Table 2 and (iii) abiotic desorption efficiencies were found to increase with increasing C_L due to greater amount of desorbed chlorophenol from mesopores. However, Table 3 shows that the amount of desorbed substrate was fairly constant at higher concentrations of loading chlorophenol solutions, suggesting the irreversible adsorption of chlorophenol onto the active sites. This amount of undesorbed chlorophenol was found to be higher for 2,4-DCP than for 4-CP and in the order of KRH > PAC > ARH > MRH for both cases.

Table 1
Characteristics of various activated rice husks and PAC

	ARH	MRH	KRH	PAC	RH
BET Plot					
S_{BET} (m^2/g)	259	200	1,465	853	1.37
R^2	0.998	0.999	0.999	0.999	0.999
Langmuir Plot					
$S_{Langmuir}$ (m^2/g)	447	269	2,989	1,610	2.12
R^2	0.997	0.999	0.982	0.988	0.989
t-Plot					
S_{micro}	190	90	849	552	
S_{meso}	69	110	616	301	
R^2	0.990	1.00	1.00	1.00	
$\%S_{micro}/S_{BET}$	73	45	58	65	
$\%S_{meso}/S_{BET}$	27	55	42	35	
V_{tot} (cm^3/g)	0.166	0.195	1.09	0.592	0.0063
V_{micro}	0.096	0.041	0.393	0.254	
V_{meso}	0.070	0.154	0.697	0.338	
$\%V_{micro}/V_{tot}$	58	21	36	43	
$\%V_{meso}/V_{tot}$	42	79	64	57	
Average pore diameter (nm)	2.56	2.89	2.98	2.77	18.3
pH_{PZC}	2.90	3.28	7.01	7.01	–

Table 2
Langmuir and Freundlich isotherm parameters for the adsorption of 4-CP and 2,4-DCP onto various activated rice husks and PAC, respectively, at 298 K

Adsorbate	Model	Parameter	MRH	ARH	KRH	PAC
4-CP	Langmuir	q_m (mg/g)	59 ± 7	66 ± 0	484 ± 14	268 ± 4
		K_L (L/mg)	0.017 ± 0.001	0.020 ± 0.001	0.063 ± 0.002	0.106 ± 0.004
		R^2	0.977	0.989	0.979	0.997
	Freundlich	K_F [(mg/g)(1/mg)$^{1/n}$]	7 ± 1	8 ± 0	181 ± 4	118 ± 1
		N	2.9 ± 0.1	2.8 ± 0.0	6.0 ± 0.3	6.9 ± 0.1
		R^2	0.993	0.995	0.946	0.978
2,4-DCP	Langmuir	q_m (mg/g)	81 ± 1	108 ± 0	733 ± 32	375 ± 8
		K_L (L/mg)	0.031 ± 0.002	0.037 ± 0.000	0.113 ± 0.014	0.190 ± 0.014
		R^2	0.987	0.983	0.993	0.997
	Freundlich	K_F [(mg/g)(1/mg)$^{1/n}$]	13 ± 1	15 ± 0	305 ± 2	173 ± 2
		n	3.0 ± 0.1	2.8 ± 0.0	6.3 ± 0.2	6.5 ± 0.1
		R^2	0.995	0.998	0.992	0.974

For further investigation, the abiotic desorption data were fitted to the Freundlich isotherm. The reversibility of adsorption is expressed as the degree of hysteresis (w), which is defined in Eq. (4) [22]

$$w\ (\%) = \left(\frac{1/n_{ads}}{1/n_{des}} - 1\right) \times 100 \tag{4}$$

where $1/n_{ads}$ and $1/n_{des}$ are the adsorption and desorption intensities obtained from the Frendlich isotherms, respectively, and the calculated w values are presented in Table 3. Lower reversibility of adsorption of the adsorbents loaded with 2,4-DCP was revealed by their greater w values compared to those of adsorbents loaded with 4-CP. Chlorophenol-loaded PAC and KRH showed higher w values compared to MRH and ARH indicating their low regeneration potential. Low reversibility of adsorption of PAC and KRH loaded with 2,4-DCP had led to negligible desorption at C_L of 100 mg/L. In comparison, KRH showed better regeneration potential compared to the PAC. This may be plausibly explained by the additional chemical activation treatment of KRH, which created greater

Table 3
Desorption efficiencies, degree of hysteresis, *w* (%), and the amount of undesorbed chlorophenols of 4-CP and 2,4-DCP, respectively, onto various activated rice husks and PAC at different initial loading concentrations, C_L

	4-Chlorophenol			2,4-Dichlorophenol		
Initial chlorophenol loading concentration, C_L (mg/L)	Desorption (%)	*w* (%)	Amount undesorbed (mg/g)	Desorption (%)	*w* (%)	Amount undesorbed (mg/g)
MRH						
50	46.3 ± 0.3	9.3 ± 3.6	5.3 ± 0.0	27.6 ± 1.0	78 ± 0	8.2 ± 0.1
100	62.0 ± 0.0	4.1 ± 2.2	5.8 ± 0.1	36.8 ± 0.2	54 ± 1	13.1 ± 0.1
200	67.4 ± 0.7	9.2 ± 5.3	7.9 ± 0.1	51.8 ± 0.4	49 ± 3	17.6 ± 0.4
300	72.5 ± 0.4	5.4 ± 0.4	8.2 ± 0.3	54.9 ± 0.4	75 ± 3	21.5 ± 0.3
400	75.8 ± 0.4	1.57 ± 0.08	8.2 ± 0.1	59.6 ± 0.3	54 ± 2	23.1 ± 0.2
ARH						
100	63 ± 10	14.6 ± 1.2	7.4 ± 2.0	18.3 ± 1.0	58 ± 0	20.1 ± 0.3
200	68.0 ± 0.0	14.6 ± 0.2	10.3 ± 0.0	30.6 ± 0.3	21 ± 4	33.4 ± 0.1
300	73.3 ± 0.3	18.2 ± 1.3	10.8 ± 0.3	41.1 ± 0.2	25 ± 2	39.8 ± 0.1
400	70.5 ± 0.7	10.1 ± 2.7	16.9 ± 0.3	48.0 ± 0.0	28 ± 2	43.5 ± 0.1
KRH						
100	22.1 ± 0.8	30 ± 12	176 ± 2	2.4 ± 0.2	–	234 ± 0
200	35.7 ± 0.8	28.6 ± 7.0	197 ± 6	19.7 ± 0.5	61 ± 13	363 ± 2
300	40.3 ± 0.9	29.6 ± 8.9	203 ± 3	28.2 ± 0.5	88 ± 6	409 ± 6
400	46.3 ± 0.3	20.3 ± 0.8	187 ± 5	32.1 ± 0.5	90 ± 7	427 ± 3
500	50.6 ± 1.1	13.7 ± 6.4	201 ± 13	35.8 ± 0.5	75 ± 3	415 ± 6
PAC						
100	7.8 ± 0.3	58 ± 9	112 ± 0	0.68 ± 0.13	–	124 ± 0
200	31.5 ± 0.0	23.6 ± 1.5	138 ± 0	7.7 ± 0.2	248 ± 19	230 ± 1
300	38.3 ± 0.0	26.2 ± 0.2	145 ± 0	19.7 ± 0.0	138 ± 3	260 ± 0
400	44.0 ± 0.2	20.4 ± 0.7	136 ± 1	25.3 ± 0.1	128 ± 0	269 ± 3
500	45.2 ± 0.1	20.9 ± 0.2	143 ± 0	29.4 ± 0.4	101 ± 16	268 ± 9

amount of mesopores. In comparison, PAC which was only thermally activated showed higher microporosity (Table 1), which contributes to adsorption with high adsorption energy and thus low desorption efficiency.

3.3. Bioregeneration efficiency

The bioregeneration efficiencies of 4-CP- and 2,4-DCP-loaded adsorbents were calculated based on Eq. (2) and the results are shown in Table 4. Despite large differences in the abiotic desorption efficiencies among the chlorophenol-loaded adsorbents as shown in Table 3, it was observed that the bioregeneration efficiencies were comparable among the chlorophenol-loaded adsorbents and the values were all above 80% except for the 2,4-DCP-loaded KRH. Many researchers [26,27,29,30] have contended that the renewal of adsorptive sites during bioregeneration was achieved by biologically induced desorption attributed to the buildup of concentration gradient between the adsorbent and bulk solution as the concentration of dissolved substrate was reduced by biodegradation. However, this mechanism was found to be inadequate to explain the attainment of relatively high percentages of bioregeneration for the chlorophenol-loaded adsorbents despite their much lower abiotic desorption efficiencies, especially for the cases of KRH and PAC. The enhanced desorption efficiency by bioregeneration could be plausibly explained by the occurrence of the exo-enzymatic biodegradation on the surface of adsorbents followed by the desorption of the products [31]. Klimenko et al. [32] reported that the adsorbents with mesoporosity would make the adsorbate more accessible to the degrading bacteria and thus would enhance the bioregeneration efficiency. Based on this mechanism, the renewal of adsorptive sites could be achieved when the microbial products were desorbed from the adsorbents. Therefore, both the mesoporosity volume and the adsorption reversibility are the main factors affecting the extent of bioregeneration.

Table 4
Bioregeneration efficiencies of the adsorbents loaded with 4-CP and 2,4-DCP

	Bioregeneration efficiency (%)	
Adsorbent	4-CP	2,4-DCP
MRH	85 ± 4	86 ± 2
ARH	81 ± 1	86 ± 1
KRH	84 ± 3	78 ± 2
PAC	86 ± 2	80 ± 4

3.4. Reusability of bioregenerated adsorbents

The total capacity loss in each cycle was determined using Eq. (3) and the values of 4-CP-loaded and 2,4-DCP-loaded adsorbents in various cycles of use are shown in Fig. 3. It was observed that total capacity losses for all the chlorophenol-loaded adsorbents increased with increasing number of cycles of use. The deterioration in adsorption capacity with increasing number of cycles of use could be due to chemical and microbial fouling [19]. The more gradual loss in the adsorption capacities for 4-CP-loaded adsorbents compared to those of 2,4-DCP-loaded adsorbents might be due to greater desorption of exoenzymatic biodegradation products of 4-CP from the adsorbents surfaces. Among the adsorbents, greater total capacity loss and thus shorter service life was observed for KRH and PAC. This could be explained by greater amount of mesopores (accessible to microorganisms) being blocked by bacteria debris resulting in the inhibition of the subsequent biodegradation process.

3.5. Comparison of the efficacies of adsorbents

Most of the literature reviews suggested that the adsorbents with higher regeneration potential should

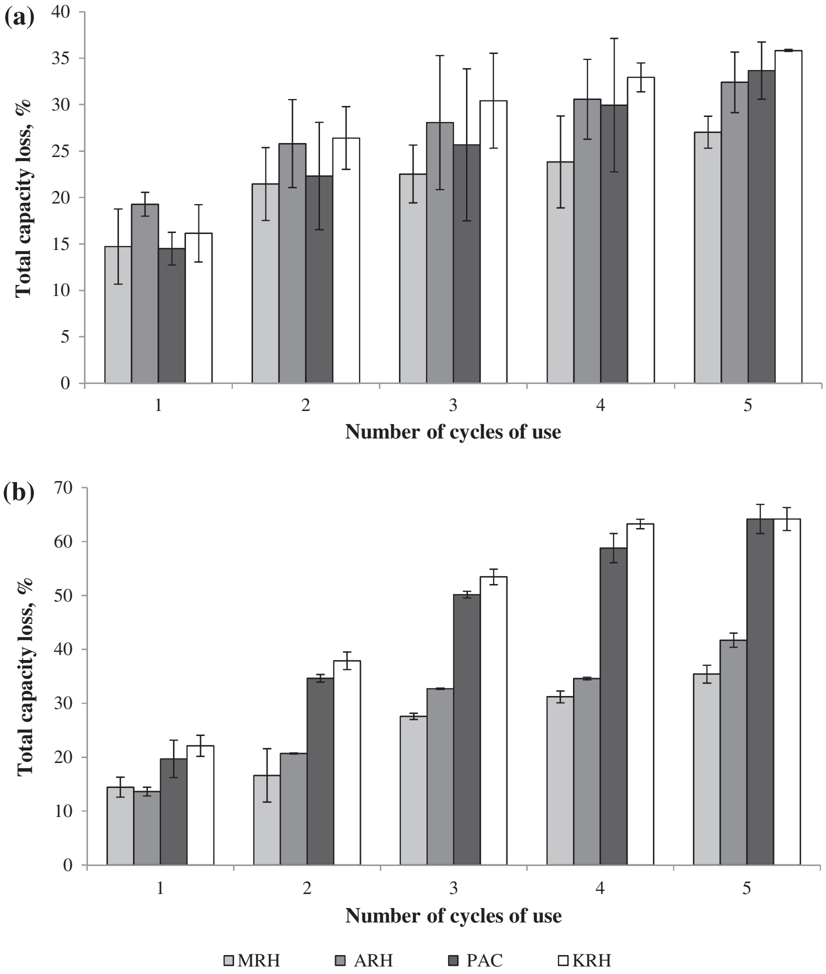

Fig. 3. Total capacity losses of (a) 4-CP-loaded and (b) 2,4-DCP-loaded adsorbents in various cycles of use.

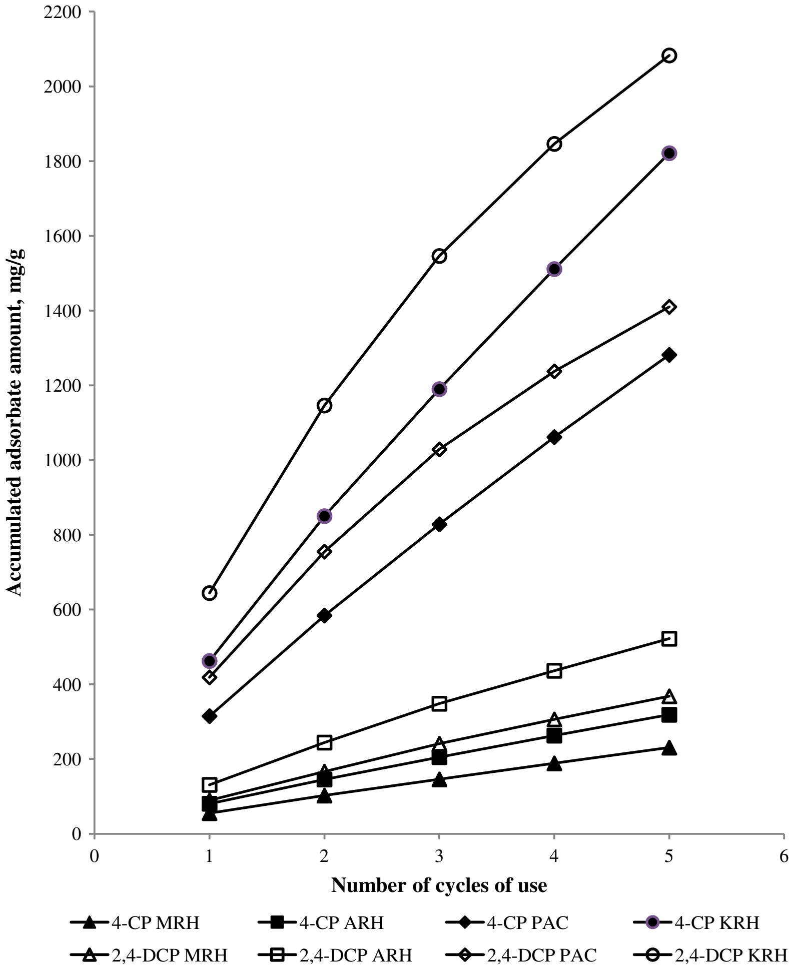

Fig. 4. Accumulated adsorbate amounts for the 4-CP-loaded and 2,4-DCP-loaded adsorbents in various cycles of use.

be chosen compared to the adsorbents with higher adsorption capacity because the former will give longer service life [16,22,33–36]. However, the researchers did not investigate the accumulated adsorbent amount after successive regeneration cycles. Fig. 4 shows the accumulated amount of adsorbate removed through adsorption using different adsorbents after various cycles of use. It was observed that, for the same adsorbent, the accumulated amount of 2,4-DCP removed was always higher than that of 4-CP after each cycle of use in line with the adsorption capacity results. In terms of the efficacy of adsorbent, the trend of accumulated amount of adsorbate removed was KRH > PAC > ARH > MRH. Thus, in spite of a shorter service life, KRH was found to be the best adsorbent with the accumulated amount of 2,4-DCP and 4-CP removed amounting to 5.7 and 7.6, 4.0 and 5.6, and 1.5 and 1.4 times higher than those of MRH, ARH, and PAC, respectively.

4. Conclusions

Among various activated rice husk-based adsorbents for the removal of 4-CP and 2,4-DCP, KRH showed the highest adsorption capacity compared to ARH and MRH due to its high surface area. For one-cycle bioregeneration, comparable bioregeneration efficiencies were observed for all the adsorbents despite the low abiotic desorption efficiencies of KRH and PAC. This can be plausibly explained by the occurrence of surface exo-enzymatic reaction which mainly happened in the mesopores. Despite greater total capacity loss with increasing number of cycles of use observed for KRH and PAC, thus indicating their shorter service period compared to ARH and MRH, KRH was still found to be the most efficient adsorbent to remove 2,4-DCP and 4-CP based on the accumulated adsorbate amount removed after successive cycles of bioregeneration.

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