

CONVERSION OF WOOD WASTE INTO ACTIVATED CARBON AND ITS APPLICATION

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ABSTRACT: This study investigated a clean technology that converts organic waste into valuable products for environmental applications. A two-step chemical activation technique of carbonization and phosphoric acid activation was investigated for activated carbon production from wood waste. The physical properties and surface chemistry of the activated carbon were determined by elemental analyses, scanning electron microscopic (SEM) imaging, BET-N₂ adsorption, Boehm's titration, and Fourier-transform infrared spectroscopy (FTIR). The wood waste-derived activated carbon possessed physical properties (surface area and pore volume) that were comparable to those of a widely used commercial activated carbon (Calgon Filtrasorb® 400), but displayed distinctive surface chemistry in terms of acidity/basicity and functional groups. Its application, for example, to industrial wastewater treatment was assessed by conducting batch adsorption study of three different classes of dyes. The fast kinetics and high adsorption capacity demonstrated the effectiveness of wood waste-derived activated carbon due to its physical properties. On the other hand, varying pH effects on the adsorption of different dyes indicated the importance of surface chemistry of activated carbon. Therefore, it is plausible that, using a range of organic waste materials and different activation schemes, activated carbon with particular physical and chemical properties can be produced for selective adsorption of priority contaminants.

INTRODUCTION

In New Zealand, a number of persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) had been widely used, resulting in localised contamination of sediments at harbours and estuaries and soils at gasworks and petroleum industry sites (Ministry for the Environment, 1997, 1999). These contaminated soils/sediments may act as long-term contamination sources to groundwater and surface water, and in turn, pose potential risks to ecosystem and humans. In recent years, concerns over the limited effectiveness of dredging and rapidly increasing disposal cost of excavated soils/sediments at hazardous waste landfill have fostered the development of in situ remediation strategies (Peters, 1999; National Research Council, 2007).

Activated carbon, a type of carbonaceous substances manufactured by well-controlled processes that develop high porosity and surface area, has been employed in ex situ stabilization of soils contaminated by PCBs, chlorophenols, and trichloroethylene (followed by solidification) in full-scale remediation (Calgon, 2004). The application of activated carbon has been recently extended to in situ stabilization (which does not require dredging, solidification, and disposal at landfills) of marine and freshwater sediments contaminated by PCBs and PAHs (Zimmerman et al., 2004; Werner et al., 2005). In these laboratory- and pilot-scale studies, aqueous concentrations and bioavailability of the organic contaminants were significantly reduced through repartitioning (phase transfer) of the contaminants from

water and sediments into the activated carbon (0.7-3.4 weight percent) (Cho et al., 2007; Sun and Ghosh, 2007; McLeod et al., 2008). This novel in situ approach using activated carbon provides a cost-effective management option for the contaminated land.

Commonly used raw materials for the production of commercial activated carbon include coal, coconut shell, wood, and petroleum coke. There is an increasing interest in producing activated carbon from organic wastes with high carbon content, such as agricultural wastes (Daifullah and Girgis, 1998; Diao et al., 2002), municipal wastes, and sewage sludge (Nakagawa et al., 2004; Zhang et al., 2005). In New Zealand, despite the fact that the uptake in recycling has increased significantly over the last decade as a result of major recycling and recovery initiatives such as composting and land application, significant proportions of waste that currently go to landfill can be utilized for activated carbon production. In particular, construction-related timber waste (14% of total waste to landfill) and organic waste (23% of total waste to landfill), including agricultural waste, sewage sludge and garden waste (Ministry for the Environment, 2007) are potentially promising precursor materials.

World demand for activated carbon is forecasted to expand 5.2 percent per year through 2012 to 1.2 million tons. Activated carbon demand would benefit from a continuing intensification of the global environmental movement as well as rapid industrialization in much of the developing world (Freedonia Group Inc., 2008). The prices of activated carbon vary (1-2 USD per pound) with its physicochemical properties, available supply at different locations, demanded quantity, etc. However, virtually all commercial activated carbon are manufactured for liquid phase and gas phase applications while there is no tailor-made product specific to the application for contaminated site remediation.

This study investigated the conversion of wood waste by means of phosphoric acid activation under varying conditions and employed the synthesized activated carbon for dye adsorption in batch experiments as a demonstration. This study is expected to be expanded to recover other major organic wastes such as dewatered sewage sludge, as a single component or mixtures, to produce activated carbon particularly effective for in situ stabilization of contaminated soils/sediments in New Zealand.

MATERIALS AND METHODS

Production of Activated Carbon from Wood Waste

The wood waste pallets in shipping industry were obtained from a container terminal in Hong Kong, where daily generation of domestic, commercial, and industrial wood wastes was 347 tons, of which 89% was discarded at landfills (Hong Kong Environmental Protection Department, 2005). Preliminary study revealed that physical activation techniques using steam or carbon dioxide were ineffective, resulting in low surface area and pore volume of the activated carbon. Thus, phosphoric acid was employed as an activating agent for chemical activation. In order to achieve more effective activation and reduce the required time, carbonization of the wood waste was performed prior to phosphoric acid activation. About 300 g of the wood waste pallets that had been sliced into small pieces and dried at 105 °C for 24 h were carbonized by partial combustion at 300 °C in a furnace (Carbolite CSF 1100) with a constant nitrogen gas flow of 250 mL min⁻¹ for 3 h at a heating rate of 4.5 °C min⁻¹, followed by cooling down with a continuous flow of nitrogen gas. The carbonized wood (charcoal) was then crushed through a 180-µm sieve.

Four sets of experiments were run in sequence with respect to each activation condition, under an implicit assumption that the conditions are independent and non-interacting

parameters. A 10 g of carbonized wood powder was firstly impregnated with phosphoric acid solution (20, 36, or 60%) at a designated impregnation ratio, i.e., phosphoric acid to carbonized wood mass ratio (1, 1.5, 2, 2.5, or 3) for 2 h. The mixtures were heated to certain activation temperatures (450, 500, 550, 600 °C) for different durations (1, 1.5, 2, or 2.5 h) in a furnace with nitrogen gas purging at 250 mL min⁻¹ with a heating rate of 7.8 °C min⁻¹, and cooled to room temperature afterwards. Excess phosphoric acid was removed and recycled from the carbon using a Soxhlet extraction system. The synthesized activated carbon was dried at 105 °C and stored in a desiccator. The activated carbon yield was about 27% (by mass) of the wood waste in this study.

Physical Properties

Microscopic images of the wood waste and the synthesized activated carbon were obtained using Scanning Electron Microscope (JEOL-6300 SEM). The physical properties (i.e., surface area and pore structure) of the activated carbon were determined by the nitrogen gas adsorption at 77K using a Brunauer, Emmett, Teller (BET) surface area analyzer (Coulter SA-3100). The samples were degassed at 120°C in vacuum for 1.5 h prior to the adsorption measurements. Nitrogen adsorption isotherms were measured at a relative pressure (P/P_0) ranging from approximately 0.001 to 0.995. The BET surface area (S_{BET}) was calculated by applying the BET equation to the adsorption data ($P/P_0 = 0.05-0.35$) and the total pore volume (V_{total}) by the Dubinin-Raduskhevich equation at $P/P_0 = 0.9814$. The micropore volume ($V_{micropore}$) was obtained by the t-plot method.

Surface chemistry

The surface acidity and basicity (i.e., acidic and basic surface groups) of the activated carbon were determined using Boehm's titration (Boehm, 1994). The numbers of acidic groups were calculated under the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups; Na₂CO₃ neutralizes carboxylic and lactonic groups; while NaHCO₃ neutralizes only carboxylic groups. The number of surface basic groups was calculated from the amount of hydrochloric acid that reacted with the carbon. A 0.15 g carbon sample was placed respectively in 20 mL of each of the following 0.05 M solutions: sodium hydroxide, sodium carbonate, sodium bicarbonate, and hydrochloric acid. The samples were sealed and allowed to equilibrate for 96 h in a rotary shaker. Each filtrate (5 mL) was transferred for titration of the excess of the base or acid with HCl or NaOH, respectively. In addition, Fourier-transform infrared (FTIR) spectroscopy was used to characterize the surface functional groups. The transmission FTIR spectra were collected using a FTIR spectrometer (Perkin Elmer Spectrum BX, USA) by averaging 32 scans in the 400–4000 cm⁻¹ spectral range at 4 cm⁻¹ resolution. The wood waste and activated carbon were homogenized with KBr at a mass ratio of 1:99 to prepare pellets using a hydraulic press at the same pressure and time.

Batch Adsorption Experiments

The synthesized activated carbon, shaken in water for 30 min prior to use to remove trapped air pockets in pores, were applied to adsorb four water-soluble dyes (Sigma-Aldrich): methylene blue (MB, basic dye), acid blue 25 (AB, acid dye), acid red 151 (AR, acid dye), and reactive red 23 (RR, reactive dye). A 0.5 g of activated carbon was mixed with 100 mL of dye solution using an orbital shaker at 400 rpm at room temperature. The mixtures were filtered after various reaction times. The dye concentrations in the filtrate were determined using a UV-visible spectrophotometer (Ultraspec 4300 pro, Denmark) at respective wavelengths of maximum absorbance. The adsorption kinetics was studied using 3000 mg L⁻¹ dye solution. A 50-h equilibrium time was used to study the pH effect. The average values of duplicate experiments were reported.

RESULTS AND DISCUSSION

Physical Properties of Activated Carbon

A comparison of SEM images of the wood waste and the synthesized activated carbon (Figure 1) illustrates that phosphoric acid activation generated a highly porous and platelet structure. This reflects that randomly oriented basic structural unit of carbons in wood waste were re-oriented in parallel (i.e., local molecular orientation) during the activation process.

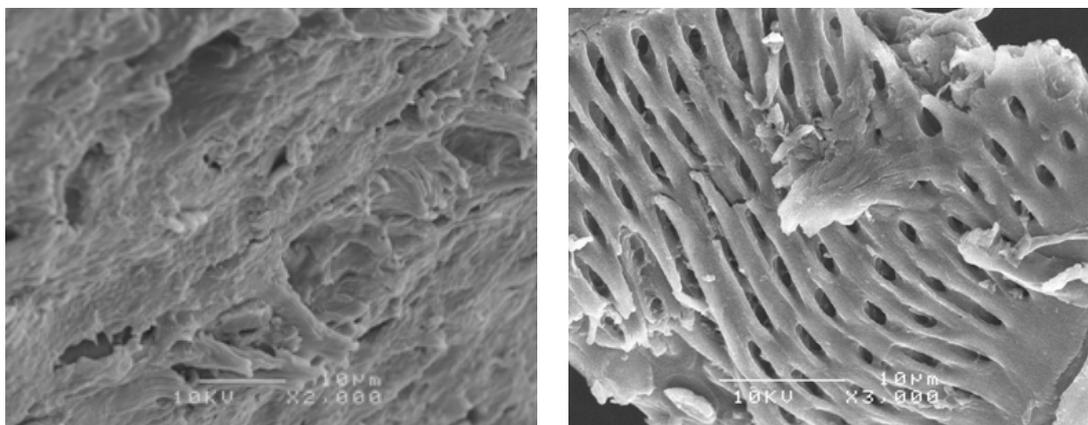


FIGURE 1. SEM images of wood waste (left) and synthesized activated carbon (right).

Varying the phosphoric acid concentration, impregnation ratio, activation temperature, and activation time, respectively, led to similar parabolic variations of SA_{BET} (Figure 1). The values of SA_{BET} were greater with an initial increase in each of these parameters (i.e., phosphoric acid concentration from 20 to 36%, impregnation ratio from 1 to 1.5, activation temperature from 450 to 550°C, activation time from 1 to 1.5 h), but then became smaller with a further increase. There may be two contrary processes in action during activation: development of pores and breakdown of the pore wall, of which the former increases the SA_{BET} while the latter decreases. It appeared that the pore volume establishment outweighed the collapse of pore walls at some point, resulting in maximum surface area as observed.

The $V_{micropore}:V_{total}$ ratio, which reflects the pore size distribution, did not substantially correlate to the phosphoric acid concentrations or activation times, but it decreased from 61 to 52% and from 64 to 48%, respectively, with an increasing impregnation ratio from 1 to 3 or activation temperature from 450 to 600°C. Such changes corresponded to a shift in pore size distribution from micropores to mesopores and macropores. A higher impregnation ratio or activation temperature, thus, is able to expand (open up) the porous structure and create more mesopores and macropores in the synthesized activated carbon. The pore size distribution would influence the extents of direct site competition and pore blockage by co-existing contaminants and natural organic matter (Li et al., 2003).

It should be noted that the effectiveness of activated carbon for in situ stabilization of PCB-contaminated sediments heavily relies on high specific surface area that is available for contaminant adsorption and fast diffusion kinetics that facilitates contaminant mass transfer into the activated carbon (Zimmermann et al., 2004; Millward et al., 2005). The fact that, under optimum activation conditions (i.e., using 36% phosphoric acid at an impregnation ratio of 1.5 to heat the wood waste at 550°C for 1.5 h), the physical properties (i.e., surface area and pore volume) of the wood waste-derived activated carbon were comparable to those of commercial activated carbon, F400 (Table 1), provides a strong ground for subsequent investigation into surface chemistry and dye adsorption.

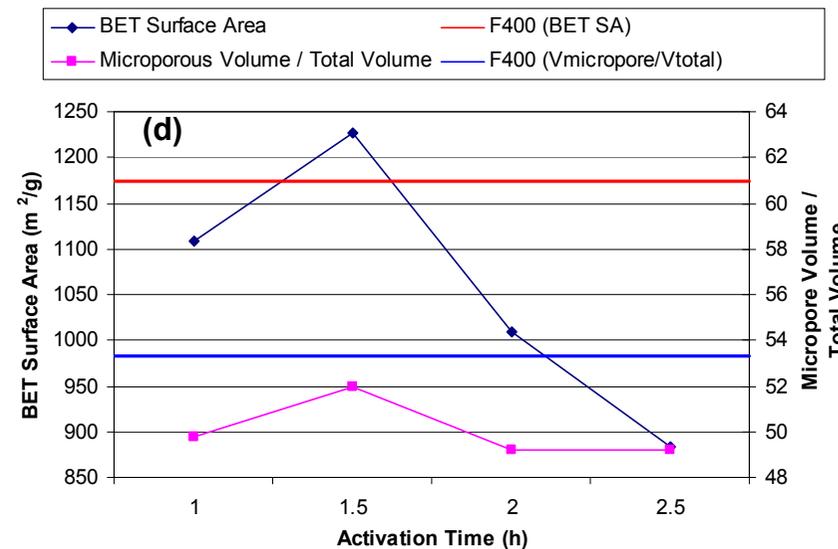
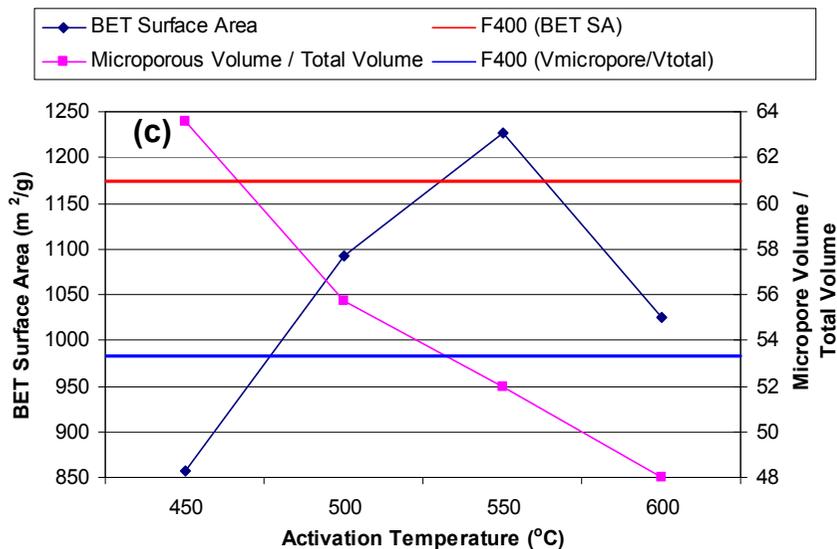
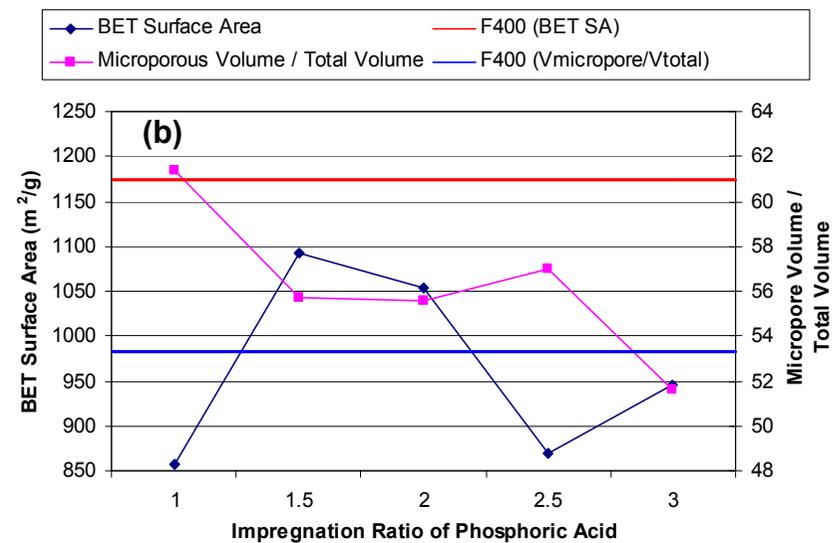
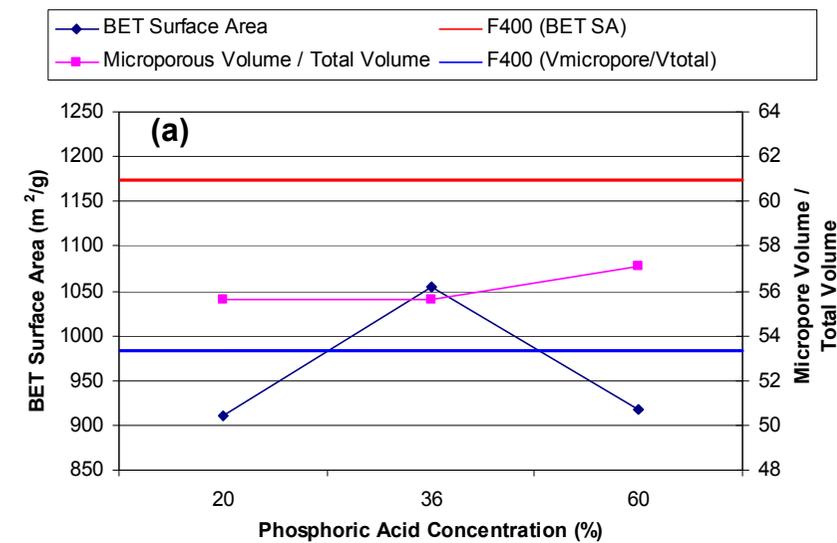


FIGURE 2. Physical properties of activated carbon derived from wood waste under different activation conditions: (a) phosphoric acid concentrations; (b) impregnation ratios; (c) activation temperatures; and (d) activation times.

TABLE 1. Comparison of physical properties of activated carbons

	F400	PAC
BET surface area (m ² /g)	1174	1211
Micropore surface area (m ² /g)	718	738
Total pore volume (ml/g)	0.60	0.61
Micropore volume (ml/g)	0.32	0.31

Surface Chemistry of Activated Carbon

The surface chemistry of the activated carbons plays key roles in adsorption mechanisms, especially for contaminants that are of polar nature or contain functional groups (e.g., dyes). Elemental, chemical, and spectroscopic analyses were conducted to provide multiple lines of evidence on the surface chemistry of activated carbon. The elemental analysis revealed that, compared with F400, the synthesized activated carbon contained lower carbon content but higher oxygen content than (Table 1). In line with this, the synthesized activated carbon had greater negative surface charge and higher amounts of surface phenolic, carboxylic, and lactonic groups, which are oxygen-containing functional groups, in the chemical analysis (Table 3). As a result, the synthesized activated carbon possessed more surface acidity and less surface basicity.

TABLE 2. Elemental analysis (mass %) of wood waste and activated carbons (AC)

	C	H	N	S	O
Wood Waste	47.8	10.37	1.31	0	40.6
Synthesized AC	63.5	3.01	1.23	0	32.3
F400	84.6	1.63	2.35	0.71	10.7

TABLE 3. Comparison of chemical characteristics of activated carbons (AC)

	F400	Synthesized AC
Acidity (mmol/g)	0.35	2.15
Basicity (mmol/g)	0.19	0.09
Phenolic (mmol/g)	0.12	0.27
Carboxylic (mmol/g)	0.04	0.41
Lactonic (mmol/g)	0.05	0.32

The FTIR spectra further provides qualitative information about the carbon surface, with the peaks identification following Weber et al. (2006). Several peaks of the wood waste (e.g., 1022 and 2855 cm⁻¹) nearly disappeared after activation, corroborating that aliphatic carbon and carbohydrates are more easily oxidized and removed (Haghseresht et al., 1999). There were fewer peaks and weaker peak intensity in the spectra of F400, where were indicative of fewer amounts of surface functional groups. This is probably because F400 is produced from bituminous coal by physical activation using steam and carbon dioxide as activating gases at higher temperatures (800-1000°C) (Calgon, 1999). It was reported that 700°C heating completely removed carboxylic groups and 900°C heating removed almost all carbonyl groups of activated carbon (Pereira et al., 2003). Compared with chemical activation, physical activation that is used for commercial activated carbon production requires heating at higher temperatures that would result in higher energy consumption as well as less reactive

activated carbon. In addition, chemical activation using strong acid could enhance dissolution of wood preservatives (chromium, copper, and arsenic), with the residual being trapped inside the activated carbon as metal oxides after heating, minimizing the long-term risk that would otherwise be associated with wood waste disposal.

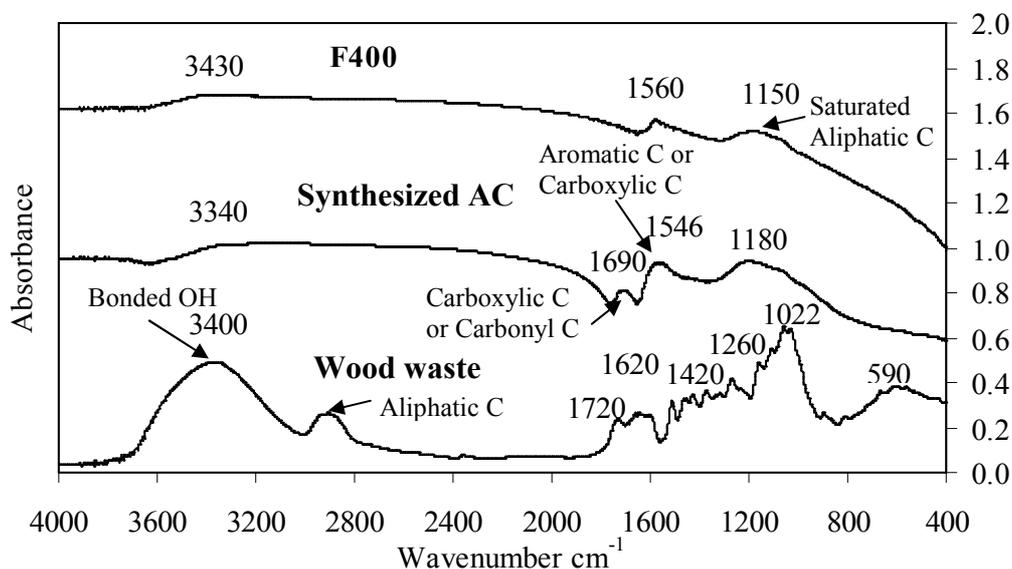


FIGURE 3. FTIR spectra of wood waste, synthesized activated carbon and F400.

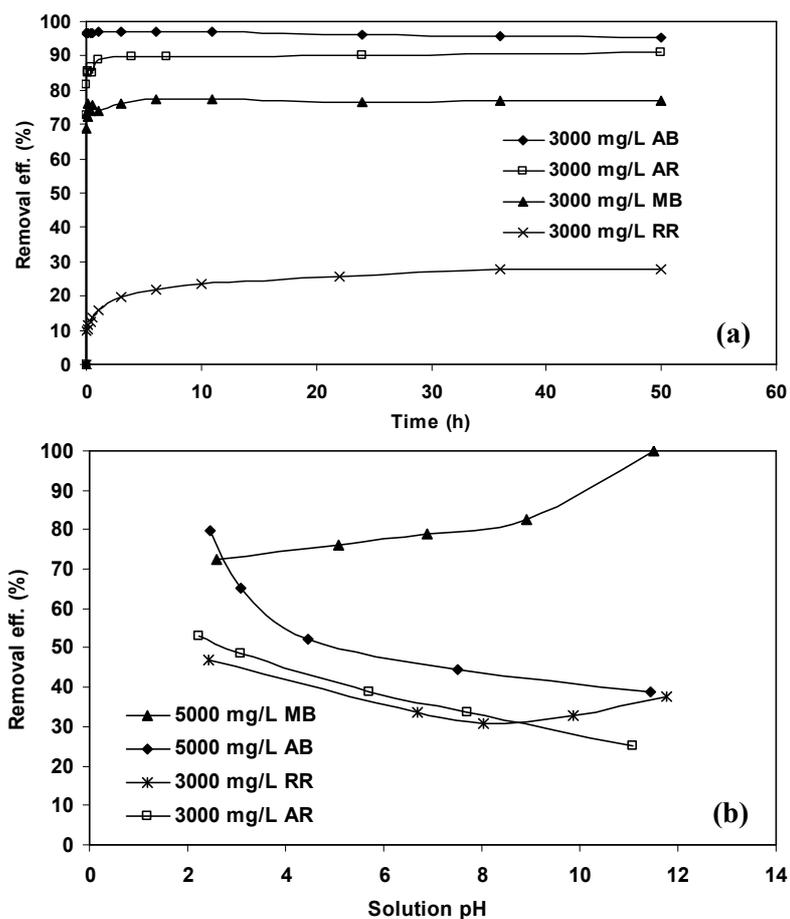


FIGURE 4. Adsorption of dyes on synthesized activated carbon: (a) kinetics and (b) effects of pH.

Batch Adsorption

The kinetics of dye adsorption (Figure 4a) was generally fast except that for the reactive dye (RR), which may be hindered by micropore diffusion or retarded surface diffusion because of its large molecular size and electrostatic attraction with the carbon surface. Figure 4b shows the effects of solution pH on dye adsorption. The surface charge of activated carbon becomes more negative with increasing pH, until reaching maximum, because of deprotonation (i.e., dissociation of H⁺ ions) of surface functional groups. In consideration of electrostatic interactions, it is not surprising that adsorption of cationic dye (i.e., basic dye, MB) positively correlated to solution alkalinity, whereas adsorption of anionic dyes (i.e., acid and reactive dyes, AB, AR and RR) negatively correlated. However, there was about 25–40% adsorption regardless of solution pH and corresponding electrostatic repulsion, indicating the occurrence of chemical adsorption of high binding strength. Chemical adsorption is particularly important for the reactive dye (RR), which contains substituent reactive groups (e.g., triazine, pyrimidine and vinyl sulphone) that can directly react with the hydroxyl groups on the surface forming covalent bond. This explains why adsorption of RR, after a decrease, increased with pH in an alkaline range as surface hydroxyl group deprotonated to a greater degree at a higher pH, allowing more formation of covalent bond with the reactive dye. The solution pH, thus, affects the degree of chemical adsorption besides electrostatic interaction. Despite not being shown, the synthesized activated carbon had higher dye adsorption capacity (except RR) than F400, suggesting that the effectiveness of activated carbon rely on surface chemistry and contaminant nature in addition to porous structure of activated carbon.

CONCLUSIONS

The effective production of activated carbon from wood waste of this study demonstrates a good potential for extension that, besides timber waste, other major organic wastes to landfill in New Zealand such as dewatered sewage sludge and gardening waste can be converted to valuable materials for environmental applications. It is plausible that activated carbon made from single or mixtures of different wastes (based on their initial compositions) under specifically designed activation conditions would possess particular physicochemical characteristics that are best for targeted engineering systems (e.g., more aromatic nature is best for sequestration of non-polar organics; more acidic/basic surface functional groups are best for sequestration of polar organics or metals). In addition to conversion to activated carbon, chemical alterations such as superheated water processing and hydrolysis may be employed to produce competitive sorbents for contaminant removal as recently investigated by Huang et al. (2006) and Weber et al. (2006). Furthermore, the efficacy of these recovered materials for in situ remediation (e.g., stabilization or reactive barriers) of contaminated site should merit further investigation.

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