Rubber Wood Sawdust Waste Converted to Activated Carbon for Heavy Metal Removal from Wastewater

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Article info

Abstract

In this study, we characterized activated carbon prepared from rubber wood sawdust waste and determined optimum conditions for removing copper ions from synthetic wastewater. Rubber wood sawdust was calcined at 600°C for 30 min and then activated with commercial vinegar (5%v/v acetic acid) or 5% lime juice for 24 hr. Three characteristics of the activated carbon were evaluated: (i) to study the ability to remove copper ions versus exposure time, pH and the amount of adsorbent, (ii) adsorption isotherms and (iii) adsorption kinetics. A Langmuir isotherm indicated that the activated carbon adsorbed a monolayer of Cu(II) ions, K_L = 7.91 mg/L with a capacity to adsorb 0.37 mg Cu(II)/g. The optimum conditions for usage was found at 20 g/L activated carbon in wastewater, pH 5 and 60 min adsorption time. Adsorption kinetics were consistent with a pseudo-second order reaction. The results of the study suggest that converting rubber wood sawdust waste to activated carbon allows it to become useful to remove heavy metal pollutants from wastewater.

Introduction

There are many environmental problems that are severe and difficult to solve. One example is sewage, contaminated with heavy metals, leaking into water supplies: water is both a resource and an important factor in the livelihood of all living things and these heavy metals are generally toxic for most life forms. Trace elements can accumulate in many stages of food chains and the ecosystem as a whole, affecting the quality of all living organisms (Renge et al., 2012). Industrial factories uses various heavy metals, including chromium, copper, nickel, zinc and wastewater from these factories contain large amounts of toxic heavy metals (Angthararuk et al.,

2022). Therefore, factories need to treat their waste effectively and monitor it for pollutants and reduce the toxicity to an acceptable amount before it is released to natural waters. Commercial considerations mean that technology for reducing heavy metal levels in wastewater must be efficient and inexpensive. A method of interest and subject of ongoing research is absorption, as it is inexpensive: an absorption system can be installed easily and quickly, as it uses normal temperature and pressure and no chemical treatment is required (Demey et al., 2018). Activated carbon adsorbents have large surface areas and high porosity and thus high adsorption capacity (Fierro et al., 2008). They can be prepared in various ways, with the main consideration being high carbon and low ash content. A low ash content indicates low concentrations of inactive material: 'activated' carbon implies sufficient surface area and pores, i.e., large absorption area (Banerjee & Mathew, 1985; Wigmans, 1989; Gergova et al., 1994; Pollard et al., 1995; Namasivayan & Kadirvelu, 1997; Kadirvelu et al., 2000). It can be formed from several natural materials – ranging from stones and seeds to husks, shells and bones (Thomas & George, 2015; Zazouli et al., 2016).

Thailand is an agricultural country and as such agricultural wastes are plentiful and scattered throughout the country, with an estimated 43 million tons per year of non-used agricultural waste (Tengkaew & Wiwattanadate, 2014). Agricultural waste can be used to produce as activated carbon, since its main constituent is carbon. It is readily available locally, cheap and environmentally friendly (Ioannidou & Zabaniotou, 2007; Saygili et al., 2015). Examples include oil palm shells (Hesas et al., 2013), rice husk (Saygili et al., 2015), sugarcane bagasse (Gurgel et al., 2008; Junior et al., 2009), coconut husks and corncobs (Tan et al., 2008). Other methods to remove heavy metals include chemical precipitation, ion exchange, chemical oxidation, reduction, reverse osmosis, ultrafiltration and electrodialysis (Fu & Wang, 2011). Recently, Muzarpar et al. (2020) and Wang et al. (2023) reviewed adsorption by activated carbon from natural sources.

Rubber plants are important crops in the Thai economy: farmers and rubber-related businesses involve at least 1 million and possibly as many as 6 million families if all related businesses are counted. Since 1991, Thailand has been the world's leading exporter of rubber and rubber products. Thailand currently faces the problem of low prices for automobile tires, a major user of natural rubber. Thus, the income of rubber farmers has been affected and the government has begun to promote the rubber wood industry. The promotion of rubber tree exports is due to the situation that in many countries the forests have been closed to cutting trees, causing a shortage of timber. As a result, rubber trees are in greater demand from Thailand. In addition to exporting rubber wood, it is still processed in the furniture industry and has experienced an increase in demand every year (Sangsuwan et al., 2019). Rubber trees that are tapped to generate natural rubber lose their efficiency with age and traditionally trees have been burnt after about 25 years. Currently the rubber trees provide further supply for the furniture industry which has caused a large amount of waste in the form of sawdust.

Therefore, the aim of this research was to show a further economic use for rubber tree sawdust such as being turned into activated carbon and applied to adsorb copper (and similar heavy metals) in wastewater. The research also focused on an economic technique to enhance pollutant adsorption using readily available commercial products. The study focused on an alternative way to add value to local agricultural waste in order to maximize economic benefits as well as environmental benefits.

Materials and methods

1. Materials

The raw materials and equipment used in this research are detailed in Table 1 and Table 2.

Table 1 The sources of raw materials

Material	Source	Note
Rubber wood sawdust	Mill, Kalasin, Thailand	16.43986°N, 103.50657°E
Cu $(NO_3)_2.3H_2O$	Carlo Erba	AR grade
NaOH	Carlo Erba	AR grade
HCl	Carlo Erba	AR grade
Acetic acid or vinegar	Commercial vinegar 5%v/v acetic acid	Local store
Lime	Commercial lime 5%v/v lime juice	Local store
Activated carbon	Chemipan Corporation Ltd.	Commercial activated carbon

Table 2 The equipment used

Item	Manufacturer
Oven	Memmert UFB400, Germany
Furnace	Carbolite RHF1600, Germany
UV-VIS spectrophotometer	Perkin Elmer Lambda 12, Germany
Scanning Electron Microscope	JEOL JSM-7800F, Germany
FTIR Spectrometer	Perkin Elmer Spectrum GX, Germany
Hotplate & Stirrer	Jenway 1103, United Kingdom

2. Preparation of activated carbon

Crushed dried rubber wood sawdust at 50 g was carbonized at 600°C for 30 min and activated with 500 mL commercial lime or acetic acid for 24 hr. The charcoal was filtered out and washed several times with distilled water until pH of the washing water was ~7. The charcoal was dried for 2 hr and incinerated (600°C, 60 min). After that, iodine adsorption analysis determined the activated carbon produced (Test D 4607, ASTM, 1998a). The prepared products were subjected to proximate analyses (ASTM, 1998b; ASTM, 1998c), morphology was examined by a scanning electron microscopy. Activated carbon was prepared at sintering temperatures from 300 to 700°C with calcination times from 30 to 180 min.

3. Wastewater preparation and standard calibration curve with Cu(II) solution

A synthetic wastewater was prepared from $Cu(NO_3)_2$.$3H_2O$-a pollutant common in industrial effluent, by dissolving 0.12 g $Cu(NO_3)_2.3H_2O$ in distilled water in a 1 L measuring flask to form a 0.5 mM solution. Cu(II) reference solutions were prepared at concentrations of 30, 40, 50, 60, 70, 80, 90, 100,110 and 120 ppm of $Cu(NO_3)_2.3H_2O$, by dilution from an initial 120 ppm Cu(II) solution. Using a UV-VIS spectrophotometer, absorbance of these solutions, at 560 nm, using a distilled water reference, formed a linear calibration curve, $R^2 = 0.9921$.

4. Adsorption studies

We assessed the effects of exposure time, pH and adsorbent loading. FT-IR spectra of the activated carbon showed relatively higher fractions of oxygenated groups (strong bands at 3340 and 1020 cm^{-1}) compared to commercial activated carbons. This result could possibly be attributed to stronger heating and drying to drive out volatile organics in the commercial products, which also showed considerably higher fixed carbon content (see Table 3).

4.1 Effect of time

To determine the optimal contact time for adsorption of Cu(II), we used the synthetic water, 0.5 mM Cu^{2+} or ~30 µg Cu/L, pH 7, an activated carbon loading of 5 g/L and exposure times of 15, 30, 45, 60, 75 and 90 min.

4.2 Effect of pH

For optimum pH determination, we used the same synthetic water and activated carbon loading and the optimum exposure time (60 min from item 4.1). The pH was adjusted with hydrochloric acid and sodium hydroxide: values were set at 3, 5, 7, 9 and 12.

4.3 Effect of adsorbent loading

For adsorbent loadings, we used the same procedure and optimum conditions, found in sections 4.1 and 4.2, with activated carbon loadings of 0.5, 1, 1.5, 2, 2.5 and 3 g. We calculated the adsorption and the adsorption capacity as follows:

$$\% \text{ Adsorption } = \left(\frac{c_o - c_e}{c_o}\right) \times 100 \tag{1}$$

$$q_e = \left(\frac{c_o - c_e}{W}\right) \times V \tag{2}$$

where C_o = initial solute concentration (mg/L), C_e = residual concentration of the solute (mg/L), q_e = amount of pollutant absorbed per gram of adsorbent (mg/g), V = solution volume (L), w = adsorbent mass (g).

5. Isotherm models

The study of copper ion adsorption kinetics with activated carbon prepared from rubber wood sawdust using concentrations of Cu(II) solutions from 60 to 100 mg/L. The activated carbon content was 0.5 g, the pH value was 5 and the exposure time was 60 min. The results were recorded on a plot graph showing the Langmuir and Freundlich adsorption isotherms.

5.1 Langmuir model

The Langmuir isotherm for monolayer adsorption assumes that only one molecule can be adsorbed on each adsorption site, each position has the same heat of adsorption and no forces act between neighbouring molecules. A model for this behaviour can be formally described in Eq. 3 which defines the amount of the adsorbate on the solid surface, q_e (Sarvestani et al., 2016; Mousavi et al., 2018; Foroutan et al., 2019) using:

$$\frac{1}{q_e} = \frac{1}{bK_LC_e} + \frac{1}{K_L} \tag{3}$$

where K_L = highest monolayer capability, C_e = metal concentration and *b* is a constant.

A plot of $\frac{1}{q_e}$ vs $\frac{1}{c_e}$ will lead to a straight line with intercept $\frac{1}{K_L}$, and slope, $\frac{1}{bK_L}$.

5.2 Freundlich model

An entirely empirical model, the Freundlich model is used for adsorption on rough surfaces, where each surface may produce varying heats of adsorption. A Freundlich isotherm assumes that q_e is proportional to a concentration raised to a 1/n power (Foroutan et al., 2019):

$$q_e = kC_e^{1/n} \tag{4}$$

where k and n are empirical constants, with q_e and C_e defined in Eq. 3. Taking logarithms of Eq. 4, the Freundlich model leads to:

$$\log q_e = \log k_F + \frac{1}{n}\log C_e \tag{5}$$

so that plotting log (q_e) vs log (C_e) at constant temperature leads to a line from which k can be derived from the y-intercept and n from the slope, which is 1/n (Foroutan et al., 2019).

6. Kinetic studies

To study copper adsorption kinetics with the activated carbon prepared from rubber wood sawdust, we used a 0.414 mM Cu (II) solution 10 mg Cu $(NO_3)_2$.$3H_2O$/L. We added 1.0 g activated carbon to a 50 mL volume, pH 5 and sampled every 15 min for 90 min. The plots for pseudo-first and pseudo-second reactions are shown in Eq. 6 and Eq. 7 (Sarvestani et al., 2016; Mousavi et al., 2018).

   6.1 Pseudo-first order kinetic model
      For first order kinetics, we expect:

$$\log (q_e - q_t) = \log q_e - k_1 t \tag{6}$$

where q_e and q_t are the amounts of copper ion adsorbed (mg/g) at equilibrium, t is time (min) and k_1 is the pseudofirstorder rate constant. The values of q_e and k_1, governing the sorption of copper ion from aqueous solution onto adsorbent, were determined from the intercept and slope of the plot of log($q_e - q_t$) *vs* t.

   6.2 Pseudo-second order kinetic model
      Second order kinetics is described by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

where, k_2 is the pseudo-second-order rate constant, determined from a plot of t/q_t vs t.

Results and discussion

1. Activated carbon preparation

The preparation of 50 g charcoal, calcined at 600°C for 30 min, was ground thoroughly and soaked with 500 mL of commercial line or vinegar for 24 hr, after which the charcoal was filtered and washed with distilled water until the wash water pH reached 7. Then 5 g charcoal

was dried for 2 hr and incinerated at 600°C for 60 min. After that, the iodine adsorption of the activated carbon was analyzed-see (Fig. 1)
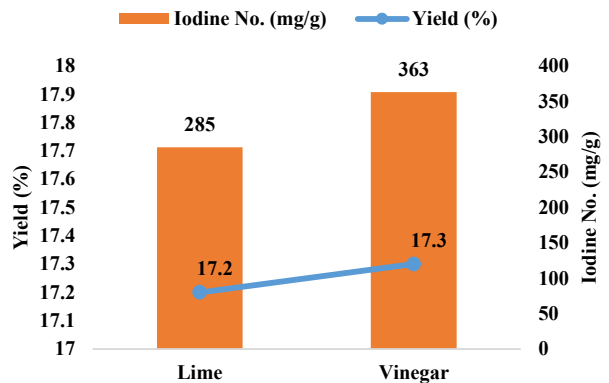

Fig. 1 Yield and iodine adsorption of activated carbon

Fig. 1 compares lime and acetic acid activation: activated charcoal with lime had an iodine adsorption value of 363 mg/g and with vinegar it was 285 mg/g. Acetic acid led to activated charcoal that was more porous than that activated by lime water. Therefore, vinegar was used to activate the carbon from rubber wood sawdust in the next process.

Fig. 2 shows iodine adsorption after activation with 5%v/v acetic acid vs calcination temperatures from 300 to 700°C for 60 min. Iodine adsorption increased with temperature leading to a maximum 366 mg/g at 600°C. A slight decrease was observed at 700°C, 344 mg/g. We attributed this to temperatures above 600°C increasing the pore size and concomitantly decreasing the active surface area. Therefore, 600°C was chosen to prepare the activated carbon for determination of the appropriate time.
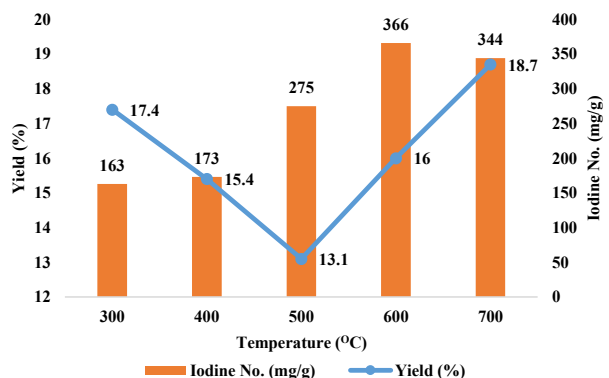

Fig. 2 Iodine adsorption and yield *vs* calcined temperature

From Fig. 3, after calcining at 600°C for up to180 min, it was found that the activated carbon prepared by incineration at 60 min had the highest iodine adsorption value, 366 mg/g. If the time was longer the iodine adsorption reduced. This was attributed to pores coalescing, so that the number and total area of pores decreased, resulting in a decrease in yield and iodine adsorption. Therefore, 60 min was chosen as the calcination time to prepare activated carbon for use in the copper ion solution adsorption experiments.
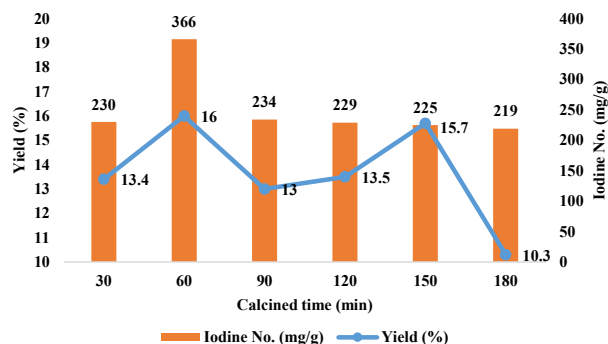
**Fig. 3** Iodine adsorption and yield *vs* calcined time

2. Properties of activated carbon from rubber wood sawdust

Table 3 shows that untreated rubber wood sawdust had the highest volatile matter content, followed by sawdust calcined (600°C, 30 min) and sawdust treated with acetic acid and re-calcined (600°C, 60 min), indicating that most of the readily degradable organics were volatile at high temperatures. This was attributed to decomposition of hemicellulose and cellulose components (Guo & Lua, 2001), whereas the ash content was inversely related to the stable carbon content. The prepared activated carbon appeared as a black powder.

Scanning electron micrographs (100 × and 1000 × magnifications) (Fig. 4) revealed the pore structure of the sawdust and activated carbon.

Table 3 Approximate composition analysis.

Type	% moisture	Approximate composition (% by weight)		
		Ash	Volatile	Fixed carbon
Untreated rubber wood sawdust	10.8	36.0	42.0	11.2
Sawdust, calcined at 600°C for 30 min	3.5	26.5	24.0	46.0
Sawdust soaked in acetic acid, 24 hr, calcined, 600°C for 60 min	2.1	24.6	20.6	52.9
Commercial activated carbon	1.0	16.4	1.4	81.2
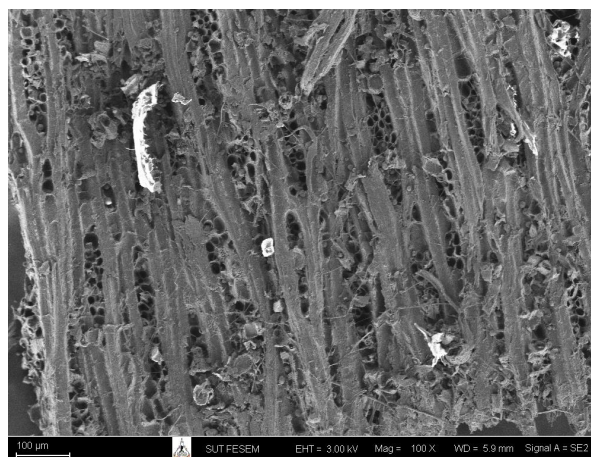
(a) Untreated sawdust,100 × mag
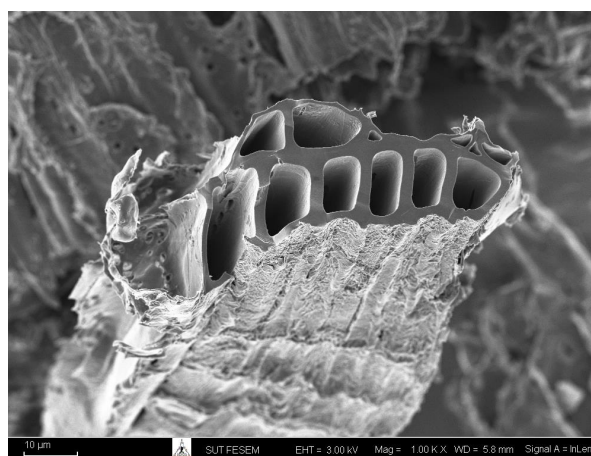
(b) Sawdust, calcined 600°C, 30 min, 1,000 × mag
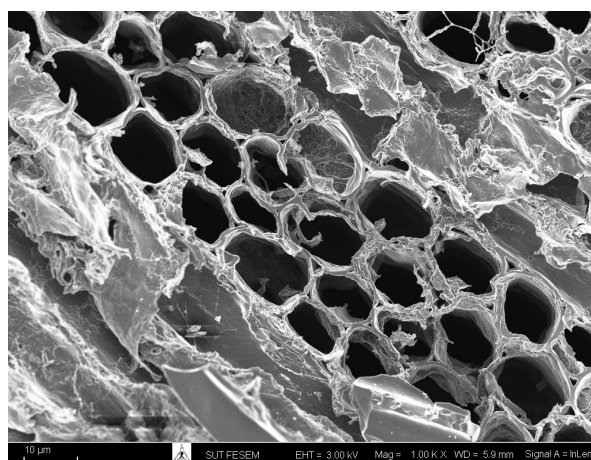
(c) Sawdust, soaked in acetic acid 24 hr, calcined 600°C, 60 min, 1,000 × mag

Fig. 4 Surfaces: raw materials and activated carbon

The surface characteristics of untreated rubber wood sawdust (Fig. 4a) differed from treated sawdust (Fig. 4b and 4c). The untreated rubber wood sawdust had a relatively flat surface and nested in layers (Fig. 4b and 4c). Sawdust, calcined at 600°C for 30 min and sawdust, soaked in vinegar for 24 hr calcined at 600°C for 60 min and had porous surfaces. The sawdust that had been calcined and soaked in vinegar had a more porous surface, attributed to acetic acid's ability to break down lignin and also destroy the cellulose crystalline structure, resulting in a more textured and porous sawdust. The increased number of pores correlated with the sorption ability. This depends on matching the pore size and the size of the adsorbent. If the adsorbent pores are smaller than the pollutant molecules sorption will be low (Al-Anber, 2010; Osu & Odoemelam, 2010). For example, Duy Nguyen et al. (2019) prepared activated carbon from sawdust for adsorption of Cu and Cd from solution. The activated carbon adsorbed Cu more strongly than Cd. Ion exchange depends partly on the atomic radius: the Cd ion radius is 9.7 nm, or larger than that of Cu, 7.3 nm. This implies that our results were consistent with the relative ionic radii (Duy Nguyen et al., 2019).
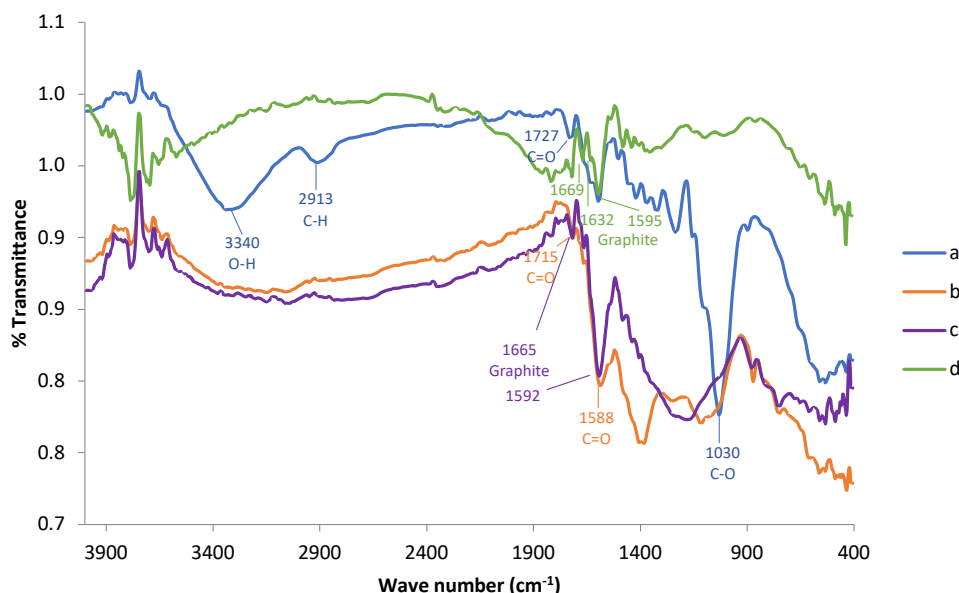
3. Infrared spectra

FTIR spectra are shown in Fig. 5. Whereas Fig. 5a shows the untreated sawdust had broad stretching peaks at 3340 cm^{-1} (O-H), 2913 cm^{-1} (C-H) and 1030 cm^{-1} (C-O in alcohol, phenol and aliphatic ether groups). Stretching for unconjugated C=O groups were seen at 1727 cm^{-1} and a strong peak at 1595 cm^{-1} was assigned to C=O attached to an aromatic ring. A peak at 1325 cm^{-1} arose from bending of the syringly group, a basic lignin component. After calcining at 600°C, OH peaks reduced significantly, the CO peak at 1030 cm^{-1} almost completely disappeared, confirming loss of alcohols, phenols and water, i.e., components which are volatile or decompose on heating. However, the C=O attached to an aromatic ring remained (peaks at 1715 cm^{-1} and 1588 cm^{-1}).

Activation with acetic acid before calcining removed some residual aliphatics (band at 1384 cm^{-1} now absent), but absorption at 1717 cm^{-1} and 1592 cm^{-1} indicated that some aromatic components remained. The commercial activated carbon exhibited small amounts of aromatics, similarly to both calcined samples but alcohols and phenols were almost absent.

The commercial activated carbon (Fig. 5d) showed peaks at 1595, 1632 and 1669 cm^{-1} assigned to carbon (graphite) and no hydroxy peaks at 3320 cm^{-1} or C-O bending peaks at 1030 cm^{-1}. Acetic acid activation resulted in a structure that closely resembled commercial activated carbon, as opposed to unactivated sawdust. Additionally, the efficacy of the acetic acid-activated product was comparable to that of commercial activated carbon, suggesting that it could potentially serve as a viable substitute for the latter.

Fig. 5 FT infrared spectra of activated carbons prepared in this study and a commercial activated carbon (a) Untreated rubber wood sawdust (b) Rubber wood sawdust, calcined 600°C for 30 min (c) Rubber wood sawdust, soaked in acetic acid for 24 hr, calcined at 600°C, 60 min (d) Commercial activated carbon

4. Adsorption capacity

The adsorption capacity of the activated carbon produced from rubber wood sawdust was evaluated under various conditions namely, the activated carbon loading, pH and time and the adsorption isotherm was determined and compared with commercial activated carbon. To study the influence of time on adsorption, the initial concentration of Cu(II) was 0.412 mM, 0.5 g of activated carbon was loaded in 100 mL, pH was 7.0 and it was shaken with an automatic shaker for 15 to 90 min.

From Fig. 6, adsorption increased rapidly with contact time to 60 min: the copper adsorption rose from an initial 7.5 to 42.5 at 60 min. At this point, it reached equilibrium and we observed a slightly reduced fraction of adsorption. The higher the contact time, the higher the adsorption value (Reza et al., 2014). This is due to the increased rate of diffusion on the surface of the adsorbent and enters equilibrium when the adsorption rate is constant (Ouyang et al., 2019).

Fig. 7 shows the effect of pH on adsorption: synthetic water, loaded with 5 g/L of adsorbent from pH 3 to 12 were adjusted with acid or base and shaken for 60 min. %adsorption *vs* pH is shown in Fig. 7.
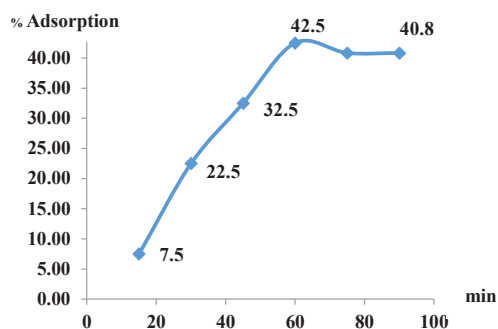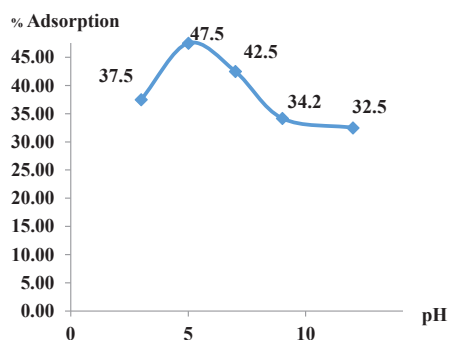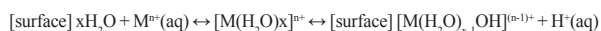
As the pH increased from 3 to 5, the copper adsorption capacity increased from 37.5% to 47.5%, but decreased for pH > 5, attributed to formation of negative hydroxyl complexes of copper at higher pH (Chen et al., 1996; Chen & Lin, 2001; Noh & Schawars, 1990).

$$[\text{surface}]\, xH_2O + M^{n+}(aq) \leftrightarrow [M(H_2O)x]^{n+} \leftrightarrow [\text{surface}]\, [M(H_2O)_{x-1}OH]^{(n-1)+} + H^+(aq)$$

These copper complexes are now larger and less able to enter pores on the activated carbon surface, reducing adsorption (Duan et al., 2016; Ajmal et al., 2003). Also, as shown by our IR spectra, the residual compounds in activated carbons vary widely with different raw materials and conditions, thus the optimum pH for copper adsorption may vary with the carbon source due to their abilities to repel Cu complexes (Al-Senani et al., 2018; Banat et al., 2002; Lorena et al., 2020; Onundi et al., 2010; Monser & Adhoum, 2002). In the Cu(II) adsorption experiment, 100 mL of the synthetic water at pH 5.0 was shaken with an automatic shaker for 60 min with activated carbon loadings varying from 0.5 to 3 g (i.e., 5 to 30 g/L).

As Fig. 8 shows, when activated carbon loading increased from 5 g to 20 g/L, adsorption increased from 47.5% to 62.5%, due to the increased activated carbon surface. However, above 20 g/L, additional adsorbent showed no benefit and may have prevented complete interaction with the solution.
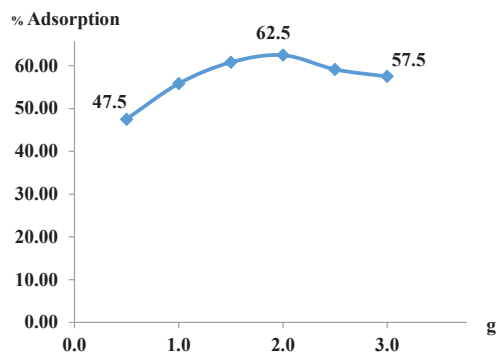
Fig. 6 Influence of Adsorption time

Fig. 8 Influence of adsorption loading (g activated carbon/100 mL)

5. Adsorption isotherms

To elucidate the underlying adsorption mechanism, Langmuir and Freundlich isotherms were compared - see Eq. 4 and Eq. 5. Copper solutions at concentrations of 60, 70, 80, 90 and 100 mg/L, activated carbon loading 5 g/L, pH 5, were shaken for 60 min. After activated carbon

Fig. 7 Influence of pH

was filtered out, the remaining copper concentration was measured in the supernatant. Data was transformed to $1/q_e$ and $1/C_e$ for the Langmuir model (Fig. 9) and log (q_e) and log (C_e) for the Freundlich model (Fig. 10).

For the Langmuir model in Fig. 9, the regression line had a slope, $1/bK_L = 0.3392$ and a y-intercept, $1/K_L = 0.1264$, $K_L = 7.91$, indicating the adsorption capacity maximum with a monolayer surface. Adsorbent ions or molecules could not cross the surface, nor bind to adjacent molecules (Taty-Costodes et al., 2003). The Freundlich model produced a regression with slope, $1/n = 2.5586$ and y-intercept, log K = 0.39. n < 1 indicated that the amount of surface adsorption was limited (Ajemba, 2014).

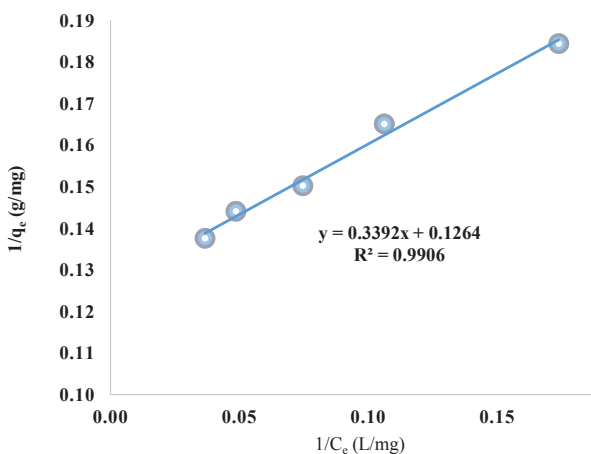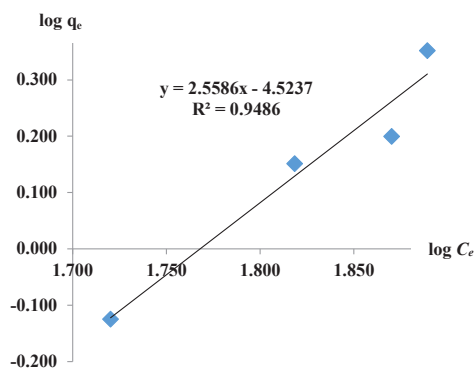The Langmuir adsorption isotherm, with $R^2 = 0.99$, was clearly a better representative of the mechanism, i.e. a monolayer of Cu^{2+} ions was formed on the surface and showed a 77% surface coverage.

Activated carbon from a wide variety of natural sources has been studied extensively, Table 4 compares critical parameters from our rubber wood derived activated carbon compared with other lignite-heavy (woody) sources. Most sources exhibited Langmuir model absorptions, but Kadirvelu et al. (2000) and Uzun & Guzel (2000) reported Freundlich adsorptions from 'commercial' sources. Although, the measured adsorption capacity is low, the process we used was extremely simple and used weak, commercially available acids, compared to the stronger and more expensive, ones, typically H_3PO_4, used by others, this lead to smaller pores restricting Copper ion adsorption.

Fig. 9 Langmuir copper adsorption isotherm

y = 0.3392x + 0.1264
$R^2 = 0.9906$

Table 4 Adsorption capacities from woody biomass sources

Study	Source	Adsorption capacity (mg/g)	Langmuir K_L (L/mg)
Kadirvelu (2000)	Commercial 'cloth'	1.1 - 8.5	0.73 - 1.08
Rafutullah (2009)	Meranti sawdust	32.1	0.05
Demiral & Ayan (2011)	Grape bagasse	37.2 - 43.5	0.11 - 0.28
Duy Nguyen (2019)	Teak wood	159 - 182	0.031 - 0.062
Lee (2019)	Gingko leaf	59.9	
Patel (2020)	Neem leaf	154	0.064
This study (2023)	Rubber wood	0.37	7.91

6. Adsorption kinetics

For assessing the adsorption kinetics, prepared 50 mL synthetic water, loaded with activated carbon 10 g/L, pH at 5, was sampled every 15 min until 90 min. Remaining Cu in the solution was measured. Data was transformed to match a first order model (Eq. 6) (Kaczala et al., 2009) and plotted in Fig. 11. Similarly, consistency with a second order model (Eq. 7) (Vadivelan & Kumar, 2005) as shown in Fig. 12.

A second order model was a better fit ($R^2 > 0.9957$) than the first order model ($R^2 = 0.7982$). This indicated that copper adsorption by activated carbon prepared from rubber wood sawdust was chemical adsorption, i.e., chemical bonds or chemical forces occurred by exchanging electrons between metal ions and the adsorbent (Semerjian, 2018).
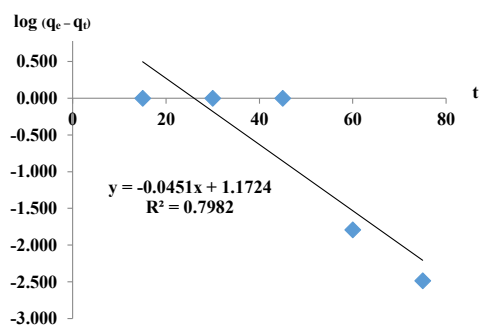

Fig. 10 Freundlich adsorption isotherm

y = 2.5586x - 4.5237
$R^2 = 0.9486$

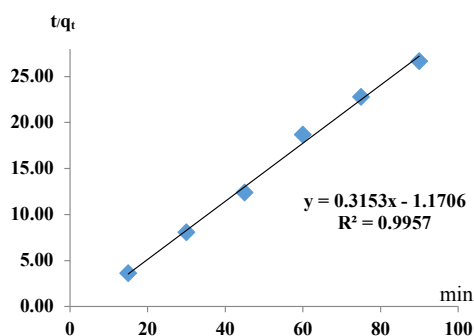**Fig. 11** Pseudo-first order model: log (q_e-q_t) *vs* t

Fig. 12 Pseudo-second order model: t/qt *vs* t

Conclusion

Optimal conditions for a simple and inexpensive process to produce activated carbon from rubber wood sawdust, where commercially available vinegar (acetic acid) showed a better activator than a lime solution. The optimum sintering needed calcining at 600°C for 60 min with acetic acid as an activator. Electron microscopy showed that this activation led to a more porous surface, because acetic acid was able to break down lignins in the raw material, leading to a 27% greater surface area, measured by iodine adsorption. The generated activated carbon was able to remove more than 40% of the Cu ions in synthetic wastewater at 5 g activated carbon per L, with removal increasing to a peak of 60% on higher loadings (20 g activated carbon/L). Comparison between Langmuir and Freundlich adsorption models supported a mono-layer adsorption pattern, i.e., a Langmuir model, with K_L = 7.91 L/g, adsorbing 0.37 g Cu(II) per g of activated carbon. Adsorption kinetics showed that a pseudo-second order model fitted the data better, hence our conclusion of per g of activated carbon that chemical bonding between Cu(II) ions and the activated carbon surface dominated.

A readily available waste such as sawdust from rubber wood furniture manufacture was converted to an effective adsorbent for metal ions in wastewater. A pre-treatment with acetic acid, from commercial vinegar, was more effective in increasing the number of pores and thus the adsorption of the activated carbon. The raw material has a negative market value, because disposing of it requires costs and burning it will create unneeded pollution, whereas converting it to activated carbon allows it to become useful to remove heavy metal pollutants from wastewater. Pretreatment requires only natural chemicals. The adsorption kinetic parameters may be used to guide larger scale commercial treatment plants.

References

Ajemba, R.O. (2014). Kinetics and equilibrium modelling of lead(II) and chromium(III) ions adsorption onto clay from Kono-bowe. *Turkish Journal of Engineering & Environmental Sciences, 38,* 455-479.

Ajmal, M., Rao, R.A.K., Anwar, S., Ahamad, J., & Ahmad, R. (2003). Adsorption studies on rice husk: removal and recovery of Cd(II) from wastewater. *Bioresource Technology, 86,* 147-149.

Al-Anber, M.A. (2010). Removal of high-level Fe³⁺ from aqueous solution using Jordanian inorganic materials: Bentonite and quartz. *Desalination, 250*(3), 885-891.

Al-Senani, G.M., & Al-Fawzan, F.F. (2018). Study on adsorption of Cu and Ba from aqueous solutions using nanoparticles of Origanum (OR) and Lavandula (LV). *Bioinorganic Chemistry and Applications, 2018,* 3936178.

Angthararuk, D., Phasuk, S., & Takolpuckdee, P. (2022). Low-cost biochar derived from bamboo waste for removal of heavy metal in aqueous solution. *Journal of Food Health and Bioenvironmental Science, 15*(2), 34-42.

ASTM Committee on Standards. (1998a). Standard test method for determination of iodine number of activated carbon. In *Annual Book of ASTM Standards* (pp.112-125). Philadelphia: ASTM Committee on Standards.

ASTM Committee on Standards. (1998b). Standard test method for total ash content of activated carbon. *In Annual Book of ASTM Standards* (pp.707-708). Philadelphia: ASTM Committee on Standards.

ASTM Committee on Standards. (1998c). Standard test method for determination of volatile matter content of activated carbon. In *Annual Book of ASTM Standards* (pp.709-711). Philadelphia: ASTM Committee on Standards.

Banat, F., Al-Asheh, S., & Al-Rousan, D. (2002). A comparative study of copper and zinc ion adsorption on to activated and non-activated date-pits. *Adsorption Science & Technology, 20*(4), 319-335.

Banerjee, S.K., & Mathew, M.D. (1985). Carbonization of jute stick. *Agricultural Wastes, 13*(3), 217-227.

Chen, J., Yiacoumi, S., & Blaydes, T.G. (1996). Equilibrium and kinetic studies of copper adsorption by activated carbon. *Separation and Purification Technology, 6*(2), 133-146.

Chen, J.P., & Lin, M. (2001). Surface charge and metal ion adsorption on an H-type activated carbon: Experimental observation and modeling simulation by the surface complex formation approach. *Carbon, 39*(10), 1491-1504.

Demey, H., Vincent, T., & Guibal, E. (2018). A novel algal-based sorbent for heavy metal removal. *Chemical Engineering Journal, 332,* 582-595.

Demiral, I., & Ayan, E.A. (2011). Pyrolysis of grape bagasse: Effect of pyrolysis conditions on the product yields and characterization of the liquid product. *Bioresource Technology, 102*(4), 3946-3951.

Duan, P., Yan, C., Zhou, W., & Ren, D. (2016). Development of fly ash and iron ore tailing based porous geopolymer for removal of Cu(II) from wastewater. *Ceramics International, 42*(12), 13507-13518.

Duy Nguyen, H.D., Nguyen Tran, H., Chao, H., & Lin, C. (2019). Activated carbon derived from teak sawdust-hydrochars for efficient removal of methylene blue, copper and cadmium from aqueous solution. *Water, 11*(12), 2581.

Fierro, V., Torne-Fernandez, V., Montane, D., & Celzard, A. (2008). Adsorption of phenol onto activated carbons having different textural and surface properties. *Microporous and Mesoporous Materials, 111,* 276-284.

Foroutan, R., Mohammadi, R., Farjadfard, S., Esmaeili, H., Ramavandi, B., & Sorial, G.A. (2019). Eggshell nano-particle potential formethyl violet and mercury ion removal: Surface study and field application. *Advanced Powder Technology, 30*(10), 2188-2199.

Fu, F., & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management, 92*(3), 407-418.

Guo, J., & Lua, A.C. (2001). Kinetic study on pyrolysis process of oil-palm stone using two-step consecutive reaction model. *Biomass and Bioenergy, 20*(3), 223-233.

Gergova, K., Petrov, N., & Eser, S. (1994). Adsorption properties and microstructure of activated carbons produced from agricultural by-products by steam pyrolysis. *Carbon, 32,* 693-702.

Gurgel, L.V.A., de Freitas, R.P., & Gil, L.F. (2008). Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by sugarcane bagasse and mercerized sugarcane bagasse chemically modified with succinic anhydride. *Carbohydrate Polymers, 74,* 922-929.

Júnior, O.K., Gurgel, L.V.A., de Freitas, R.P., & Gil, L.F. (2009). Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by mercerized cellulose and mercerized sugarcane bagasse chemically modified with EDTA dianhydride (EDTAD). *Carbohydrate Polymers, 77,* 643-650.

Hesas, R.H., Arami, A.N., Duad, W.M.A., & Sahu, J.N. (2013). Comparison of oil palm shell-based activated carbons pro-duced by microwave and conventional heating methods using zinc chloride activation. *Journal of Analytical and Applied Pyrolysis, 104,* 176-184.

Ioannidou, O., & Zabaniotou, A. (2007). Agricultural residues as precursors for activated carbon production – A review. *Renewable and Sustainable Energy Reviews, 11*(9), 1966-2005.

Kaczala, F., Marques, M., & Hogland, W. (2009). Lead and vanadium removal from a real industrial wastewater by gravitational settling/sedimentation and sorption onto Pinus sylvestris sawdust. *Bioresource Technology, 100,* 235-243.

Kadirvelu, K., Palanival, M., Kalpana, R., & Rajeshwari, S. (2000). Activated carbon from an agricultural by-product for the treatment of dyeing industry wastewater. *Bioresource Technology, 74,* 263-265.

Lee, M.E., Park, J.H., & Chung, J.W. (2019). Comparison of the lead and copper adsorption capacities of plant source materials and their biochars. *Journal of Environmental Management, 236,* 118-124.

Lorena, Al., Irene, Ga., Francisco, J., & Felix, A. (2020). Removal of copper ions from wastewater by adsorption onto a green adsorbent from winemaking wastes. *Bioresource Technology, 15*(1), 1112-1133.

Monser, L., & Adhoum, N. (2002). Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater. *Separation and Purification Technology, 26,* 137-146.

Mousavi, M., Hashemi, A., Arjmand, O., Amani, A.M., Babapoor, A., Fateh, M.A. ... & Jahandideh, S. (2018). Erythrosine adsorption from aqueous solution via decorated graphene oxide with magnetic iron oxide nano particles: kinetic and equilibrium studies. *Acta Chimica Slovenica, 65*(4), 882-894.

Muzarpar, M.S.A., Leman, A.M., Maghpor, N., Nik, N.M.H., & Norasyikin, M. (2020). The Adsorption Mechanism of Activated Carbon and Its Application - A review. *International Journal of Advanced Technology in Mechanical, Mechatronics and Materials, 1*(3), 118-124.

Namasivayan, C., & Kadirvelu, K. (1997). Activated carbons prepared from coir pith by physical and chemical activation methods. *Bioresource Technology, 62,* 123-127.

Noh, J.S., & Schawars, J.A. (1990). Effect of HNO_3 treatment on the surface acidity of activated carbons. *Carbon, 28*(5), 675-682.

Onundi, Y.B., Mamun, A.A., Al-Khatib, M.F., & Ahmed, Y.M. (2010). Adsorption of copper, nickel and lead from synthetic semiconductor industrial wastewater by palm shell activated carbon. *International Journal Environmental Science and Technology, 7*(4), 751-758.

Osu, C.I., & Odoemelam, S.A. (2010). Studies on adsorbent dosage, particle sizes and pH constraints on biosorption of Pb (II) and Cd (II) ions from aqueous solution using modified and unmodified *Crasstrotrea gasar* (Bivalve) biomass. *International Archive of Applied Sciences and Technology, 1*(1), 62-68.

Ouyang, D., Zhuo, Y., Hu, L., Zeng, Q., Hu, Y., & He, Z. (2019). Research on the Adsorption Behavior of Heavy Metal Ions by Porous Material Prepared with Silicate Tailings. *Minerals, 9*(5), 291.

Patel, H. (2020). Batch and continuous fixed bed adsorption of heavy metals removal using activated charcoal from neem (*Azadirachta indica*) leaf powder. *Scientific Reports, 10,* 16895.

Pollard, S.J.T., Thompson, F.E., & McConnachie, G.L. (1995). Microporous carbons from Moringa Oleifera Husks for water purification in less developed countries. *Water Research, 29,* 337-347.

Rafutullah, M., Sulaiman, O., Hashim, R., & Ahmad, A. (2009). Adsorption of copper (II), chromium (III), nickel (II) and lead (II) ions from aqueous solutions by meranti sawdust. *Journal of Hazardous Materials, 170*(2-3), 969-977.

Renge, V.C., Khedkar, S.V., & Pande, S.V. (2012). Removal of heavy metals from wastewater using low cost adsorbents: A review. *Scientific Reviews and Chemical Communications, 2*(4), 580-584.

Reza, R.A., Ahmaruzzaman, M., Sil, A.K., & Gupta, V.K. (2014). Comparative adsorption behavior of ibuprofen and clofibric acid onto microwave assisted activated bamboo waste. *Industrial Engineering Chemistry Research, 53*(22), 9331-9339.

Sangsuwan, S., Vuddhimethi, Y., & Jarusombuti, S. (2019). The development of rubberwood furniture industry for export of Thailand. *Journal of Humanities and Social Sciences Thonburi University, 13*(3), 77-84.

Sarvestani, F.S., Esmaeili, H., & Ramavandi, B. (2016). Modification of Sargassum angustifolium by molybdate during a facile cultivation for high-rate phosphate removal from wastewater: structural characterization and adsorptive behavior. *Biotechnology, 6,* 251.

Sayğili, H., Güzel, F., & Önal, Y. (2015). Conversion of grape industrial processing waste to activated carbon sorbent and its performance in cationic and anionic dyes adsorption. *Journal of Cleaner Production, 93,* 84-93.

Semerjian, L. (2018). Removal of heavy metals (Cu, Pb) from aqueous solutions using pine (Pinus halepensis) sawdust: Equilibrium, kinetic, and thermodynamic studies. *Environmental Technology Innovation, 12,* 91-103.

Tan, I.A.W., Ahmad, A.L., & Hameed, D.B. (2008). Preparation of activated carbon from coconut husk: Optimization study on removal of 2, 4, 6-trichlorophenol using response surface methodology. *Journal of Hazardous Materials, 153,* 709-717.

Taty-Costodes, V., Fauduet, H., Porte, C., & Delacroix, A. (2003). Removal of Cd(II) and Pb(II) ions, from aqueous solutions by adsorption onto sawdust of Pinus sylvestris. *Journal Hazardous Materials, 105,* 121-142.

Tengkaew, S., & Wiwattanadate, D. (2014). Study of source and potential of biomass from field corn in Thailand. *Prince of Naradhiwas University Journal, 6*(3), 103-111.

Thomas, B., & George, S. (2015). Production of activated carbon from natural sources. *Trends in Green Chemistry, 1,* 1-7.

Uzun, I., & Guzel, F. (2000). Adsorption of some metal ions from aqueous solution by activated carbon and comparison of percentage adsorption results of activated carbon with those of some other adsorbents. *Turkey Journal of Chemistry, 24,* 291-297

Vadivelan, V., & Kumar, K.V. (2005). Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. *Journal of Colloid and Interface Science, 286,* 90-100.

Wang, B., Lan, J., Bo, C., Gong, B., & Ou, J. (2023). Adsorption of heavy metal onto biomass-derived activated carbon: review. *RSC Advances, 13,* 4275-4302.

Wigmans, T. (1989). Industrial aspects of production and use of activated carbon. *Carbon, 27,* 13-22.

Zazouli, M.A., Azari, A., Dehghan, S., & Malekkolae, R.S. (2016) Adsorption of methylene blue from aqueous solution onto activated carbons developed from eucalyptus bark and *Crataegus oxyacantha* core. *Water Science & Technology, 74*(9), 2021-2035.