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Cr(VI) Removal by a New Biocarbon Material Prepared from Local *S. Thaipingensis* ('Pokok Gapis') Leaf Biomass: Characterization, Isotherm and Kinetic Studies

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Abstract: This study reports the preparation of a new biocarbon material from the leaf biomass of local *S. thaipingensis* tree by heat treatment for use as low cost bioadsorbent material for Cr(VI) removal. To the best of our knowledge there is no literature to date on the exploitation of this species for similar purpose. The newly prepared biocarbon had higher carbon (58.35%) and lower ash (5.98%) content than its precursor. Batch sorption experiment was carried out at varying contact time (30-300 min), biocarbon dosage (0.125-0.500 g), initial pH(2-8) and Cr(VI) concentrations (10-100 mg/L) to ascertain Cr(VI) removal capability. Results showed that 0.125 g of biocarbon material was able to remove Cr(VI) as much as 72.72±0.27 to 98.81±0.82% at 10-100 mg/L, pH 2 and 180 min of agitation time ($p<0.05$). Adsorption followed the Freundlich model ($K_f = 4.80$, $n = 2.85$, $R^2 = 0.9963$) and pseudo-second order kinetics ($R^2 = 0.9946$) implying a multilayer surface chemisorption accompanied by interactions between the adsorbed Cr on the biocarbon surface and Cr ions in the solution. SEM examination revealed pore like structures that can adsorb Cr in the biocarbon and the rich and diverse chemical functional groups (-C-H-, -C-C-, -C = C-, -C-N-, -N-H-) and oxides (Ca, Na, Si) that can facilitate adsorption were observed through FTIR and XRF analyses. This study affirms the suitability of *S. thaipingensis* leaf powder biomass as a biocarbon precursor for use as low cost bioadsorbent material for waste effluent remediation.

Key words: Adsorption, biocarbon, carbonization, heat treated, heavy metals, water pollution

INTRODUCTION

Water security has been identified as one of the critical area that needs to be addressed in nation development. Water as the prerequisite medium for life must be protected and preserved. The industry boom underlining rapid economic activities have accentuated water pollution due to the release of untreated waste effluent. Among the pollutants, heavy metals in specific hexavalent chromium, Cr(VI) is being focused as it is among the top sixteen toxic pollutants (Gupta and Mote, 2014) as a known mutagen and carcinogen and ability to exist in various oxidation states in the aqueous solution (Porozhnyuk *et al*., 2014). Contamination of the water bodies due to release of untreated Cr(VI) containing waste effluent is of serious concern. The Cr metal have vast usage in the industry among which in textile manufacturing, tanning, electrolytic coating, semi-conductors, paint, chemicals, iron and steel, etc. (Fouathia and Meziani, 2007; Joshi *et al*., 2014). The acceptable concentration limit of Cr(VI) is 0.05 mg/L in potable water (World Health Organization, 2004).

However, the concentration of Cr(VI) present in the waste effluents from industrial sites are in the range of 50-200 mg/L (Sinha *et al*., 2013). It is tasteless, odourless and cannot be degraded biologically, associates with oxygen to produce chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{-2}$) ions (Ahalya *et al*., 2005) that readily dissolves in flowing water, contaminating the source of drinking water, affects aquatic lives and accumulates in living organisms (Gupta and Mote, 2014). Therefore, we should reduce the concentration of Cr(VI) to a safe level before discharging the waste effluent into the environment. There are two main approaches in treating and remediating heavy metal containing wastes which are through the conventional approach and biological approach. The various methods include chemical precipitation, ion exchange (Ahalya *et al*., 2005; Sinha *et al*., 2013; Joshi *et al*., 2014), ultrafiltration, reverse osmosis and solvent extraction, among others (Meniai *et al*., 2007; Mohanty *et al*., 2014). However, the disadvantages of conventional methods are high cost, not effective in the removing of low concentration (1-100 mg/L) heavy metal (Sannasi *et al*., 2010;

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Gupta and Mote, 2014) incomplete removal of the metal and the production of toxic compound or waste product.

More recently, biomass material have been opted in a process called biosorption, referring to the use of biomaterials to sorb pollutants (Rao and Prabhakar, 2011). These include fungi, microbial cells in both living and dead forms (Sannasi *et al*., 2010) coconut shell, rice husk, cow dung, bean husk, leaves, sugar waste and sawdust (Wongjunda and Saueprasearsit, 2010; Sinha *et al*., 2013; Rajoriya and Kaur, 2014; Ghosh *et al*., 2015; Palsan *et al*., 2015; Sannasi and Pieter, 2016). Most of the commercial grade activated carbon is produced by a two-step process; high temperature (600-1000°C) carbonization followed by activation either by chemical (acids, bases, salts) or physical means (steam, thermal) and usually in the presence of inert gas (Makeswari and Santhi, 2013). As opposed to harder agrowaste material, the use of softer precursor materials will require lower temperature and less intense processing.

In this research, the biocarbon is produced solely through carbonization of the leaf powder biomass by heat treatment without any chemical pre-treatment or modification. Factors such as time and the temperature of carbonization (Mohamed *et al*., 2010; Trevino *et al*., 2013) greatly affect the properties, characteristics and effectiveness of the resultant biocarbon product. Hence, great care is needed in carrying out the carbonization process as too high of a temperature and time will turn the raw material into ash. Controlled carbonization can eliminate the non-essential non-carbon and other volatile compounds and increase the carbon content of the raw material.

This research focuses on the preparation of heat treated biocarbon material derived from plant refuse i.e., leaf litter, the characterization of the newly prepared biocarbon material and studies of its use as potential bioadsorbent for Cr(VI) removal. In this exploratory research, the much abundant all year round available leaf litter of *Saraca thaipingensis* (‘pokok Gapis’) have been opted as the precursor for this novel biocarbon. *S. thaipingensis* belongs to the Fabaceae family and can be widely found in the South East Asia region. Preliminary research with the raw leaf powder had been promising (Palsan *et al*., 2015) but leaf powder clumps often occurred due to hydrophobic nature of the biomass. Hence for application purpose, the carbonized form is foreseen to be more practical. To the best of our knowledge there have yet to be any research reporting on the carbonization of leaf powder biomass from this tree species. As of current, the large leaf (20-40×6-12 cm) litter waste clogs the water ways, left to rot and often put to open burning. We hope to minimize the negative effect towards the environment by reducing the waste volume by utilizing it as low cost biocarbon precursor. The objectives of this research were to prepare and characterize the new heat-treated biocarbon material to determine the effect of initial pH, contact time, biocarbon dosage and concentration towards Cr(VI) uptake and to investigate Cr(VI) removal behaviour by the heat-treated biocarbon by use of isotherm and kinetic models.

MATERIALS AND METHODS

Chemicals: All routine chemicals and reagents were of analytical grade. Stock solution containing 1000 mg/L of Cr(VI) was prepared by weighing 0.282 g of potassium dichromate, $K_2Cr_2O_7$ (R&M Marketing, Essex, UK) and dissolved in 100 mL of distilled water. Varying concentrations of Cr(VI) solutions were diluted from this stock solution by adding specific volume of distilled water. The 0.25% (w/v) of 1,5-diphenylcarbazide reagent was prepared by dissolving 0.125 g of 1,5-diphenylcarbazide into 49 mL of acetone with 1 mL of 0.2 M of sulfuric acid (H_2SO_4). The solution pH was adjusted with either 1 M of H_2SO_4 or 1 M NaOH.

Sourcing and preparation of plant leaves: The fallen dry leaves were collected around Machang, Kelantan, Malaysia. The leaves were washed thoroughly using distilled water to remove impurities and dirt and sun-dried. The leaves were grinded to powder form by using electric grinder (Brand New Cosmos Soylove II, model: SB-518). The leaf powder was sieved to obtain particle size in the range of ≤150 μm by using auto sieve shaker (Model: A060-01). The leaf powder was stored in an air-tight container.

Determining the minimum carbonization temperature: The leaf powder (~10-15.0 g) was subjected to carbonization at varying temperatures (300-800°C) for 1 h in a muffle furnace (Carbolite ELF 11/6B). The initial weight (g) of the leaf powder and the final weight (g) of the biocarbon were recorded and the percentage yield calculated as: percentage of yield = [(Initial weight-final weight)/initial weight)]×100%. The biocarbon material was stored in an air-tight container.

Characterization of the raw leaf powder and biocarbon material: Both the raw leaf powder, i.e., the precursor and the produced biocarbon material (after heat treatment) were characterized by proximate analysis of ASTM standard as described by Qian (2014), X-ray Fluorescence (XRF; Bruker S2 Ranger, Germany with Equa oxide analysis) to determine the chemical compound composition, X-ray diffraction (XRD; Bruker D2 Phaser, Germany with DIFFRAC.SUITE Software) with CuKα radiation at 40 kV/40 mA at λCu = 1.5406 Å, step size was 0.01°/sec, from 10-90° angle in 2θ to obtain their

Table 1: Experimental design for investigating Cr(VI) removal capability of the biocarbon

Test parameters	Initial pH	Dosage (g)	Contact time (min)	Initial [Cr(VI)] (mg/L)
Effect of contact time	2	0.125	30, 60, 120, 180, 240, 300	100
Effect of initial pH	2, 4, 6, 8	0.125	240	100
Effect of dosage	2	0.125, 0.250, 0.500	240	100
Effect of initial [Cr(VI)]	2	0.125	180	10, 20,40, 60, 80, 100

Table 2: Different types of isotherms

Isotherm	Formula (linearized form)	Plot	Parameters
Freundlich	$\log q_e = \frac{1}{n} \log c_e + \log k_f$	$\log q_e$ vs. $\log c_e$	$n = \frac{1}{\text{slope}}$; $K_f = \log^{-1} \text{intercept}$
Langmuir-1	$\frac{c_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max} b}$	$\frac{c_e}{q_e}$ vs. c_e	$q_{max} = \frac{1}{\text{Slope}}$; $b = \frac{\text{Slope}}{\text{Intercept}}$
Langmuir-2	$\frac{1}{q_e} = \frac{1}{b q_{max}} \frac{1}{c_e} + \frac{1}{q_{max}}$	$\frac{1}{q_e}$ vs. $\frac{1}{c_e}$	$q_{max} = \frac{1}{\text{Intercept}}$; $b = \frac{\text{Intercept}}{\text{Slope}}$
Langmuir-3	$\frac{q_e}{c_e} = -b q_e + b q_{max}$	$\frac{q_e}{c_e}$ vs. q_e	$q_{max} = -\frac{\text{Intercept}}{\text{Slope}}$; $b = -\text{slope}$

crystallographic profile, Fourier Transformed Infra-Red (FTIR; iZ10) to screen the available and changes to the chemical functional groups and electron microscopy (SEM; Hitachi S3400N SEM) to view their morphology features.

Determination of point of zero charge (pH_{pzc}): The pH_{pzc} value was determined by using the modified pH drift method as described by Smiciklas *et al.* (2000). Ten flasks of 50 mL NaCl solutions were prepared. The initial pH (pH_i) of NaCl solutions were adjusted between 1 and 10 by adding 0.1 M HCl or 0.1 M NaOH. Ten sets of 0.1 g biocarbon were weighed and poured into each of the prepared test flasks. The flasks were put on the orbital shaker (Smith A3446, China) with agitation speed of 150 rpm. The samples were allowed to equilibrate for 24 h at room temperature (25±2°C). After 24 h, the final pH (pH_f) values of the solutions were recorded. A graph of difference between the initial pH and final pH (pH_i-pH_f) was plotted against pH_i. Intersection point observed from the graph gives the pH_{pzc} (Makeswari and Santhi, 2013).

Cr(VI) analyses: The standard 1,5-diphenylcarbazide (DPC) assay was followed (APHA, 1998; Palsan *et al.*, 2015). At equilibrium time, the biocarbon was separated from the solution by filtration (Whatman No.1). The concentration of Cr(VI) in the filtrate was determined spectrophotometrically at 540 nm (Spectronic 200, Germany) and compared to a standard curve ($R^2 = 0.999$). The Cr(VI) removal of percentage is calculated as $= C^\circ\text{-}C_e/C_o \times 100$ and Cr(VI) uptake (q_e mg/g) = C_o-C_e/w×volume of solution (L) where C_o (mg/L) is the initial concentration of Cr(VI), C_e (mg/L) is the concentration of Cr(VI) at equilibrium and w is the dry weight of the biocarbon (g) (Mohanty *et al.*, 2014).

Biosorption experimental design: The comparative screening to ascertain the effect of initial pH, biocarbon dosage, particle size, contact time and varying concentration of Cr(VI) were carried out in batch mode (Table 1) at room temperature (26±2°C) and agitated at 250 rpm.

Isotherm modelling: The universal Langmuir and Freundlich isotherm models were chosen to describe the adsorption behaviour (Okeola and Odenbunmi, 2010; Gupta and Mote, 2014) of Cr(VI) by the heat-treated biocarbon. The isotherm types and their respective notations are listed in Table 2 where q_e (mg/g) is the amount of Cr(VI) adsorbed per unit mass of biocarbon at equilibrium; C_e (mg/L) is the concentration of unadsorbed Cr(VI) in solution; q_{max} (mg/g) is the maximum amount of Cr(VI) adsorbed per unit mass of biocarbon; b (L/mg) is the constant related to affinity of binding sites; 1/n is the intensity of adsorption; K_f (mg/g) is the adsorption capacity of the biocarbon (Kumar and Tamilarasan, 2013; Singanan and Peters, 2013). Freundlich isotherm proposes a multilayer biosorption with interactions between the adsorbed Cr(VI) on the surface of biocarbon and the Cr(VI) in the solution. Langmuir isotherm on the other hand proposes a monolayer biosorption without interaction between the adsorbed Cr(VI) on the surface of biocarbon and the Cr(VI) in the solution.

Data analyses: All tests were done in triplicates (n = 3) and the Mean±Standard Error (SE) or Deviation (SD) is reported. The data were subjected to Analysis of Variance (ANOVA), Fischer's LSD Post Hoc and Duncan's test. Significance level was set at 95% ($\alpha = 0.05$).

RESULTS AND DISCUSSION

Determining the minimum carbonization temperature: It was observed that at 500°C and above, ash (white deposits) appeared in the biocarbon powder indicating

Table 3: Comparing the properties of the raw leaf powder of and the biocarbon *S.thaipingensis*

Sample/Factors	Values
Raw leaf powder	
pH	7.70
Ash (%)	8.78
Volatile matter (%)	75.33
Moisture (%)	7.04
Fixed carbon (%)	47.62
Biocarbon material	
pH	7.30
Ash (%)	5.98
Volatile matter (%)	45.29
Moisture (%)	4.04
Fixed Carbon (%)	58.35

burned leaf powder. In contrast at temperatures below 300°C, the leaf powder were brownish in colour reflecting incomplete carbonization. Complete carbonization and the minimum carbonization temperature was read at 450°C and heating time of 1 h with an optimum yield of 40.96±0.10%. The significant weight loss was attributed to the loss of moisture and volatile matter from the raw leaf powder.

Characterization of the raw leaf powder and biocarbon material: The characterization results are summarized in Table 3. The pH value of the raw leaf powder is 7.7 whereas the pH value after heat treatment is 7.3. The moisture content of the raw leaf powder is 7.04% but after heat modification, the moisture content decreased to 4.04%. Lower moisture content is preferred as the presence of water will result in high moisture content which can affect the adsorption process and adsorption capacity. There is a slight decrease in the volatile matter content from 75.33-45.29%. The onset of carbonization by heat treatment would have removed all the heat-labile compounds and produce a more stable carbon concentrated compound material. As expected fixed carbon content increased from 47.62-58.35% whereas percentege of ash decreased from 8.78-5.98% after heat treatment. According to Mohamed *et al*. (2010), a precursor with a high fixed carbon and low ash content are potential candidates to be developed and used as bioadsorbents to remove pollutants.

Table 4 presents the chemical compound composition of the raw leaf powder and the newly produced biocarbon obtained through XRF analysis. The composition of the leaf powder was reflective of natural biological material with the presence of earth and alkali earth metals. There were no significant difference between the two samples though the concentration of the compounds mostly decreased in the heat treated material. Heat treatment did not change the composition of the precursor material in total. Chromium, its oxide or any other heavy metal compounds were not detected in both samples. The three highest compounds were CaO (42.50-47.8%) followed by Na_2O (18.5-20.80%) and SiO_2 (13.10-13.40%). Interestingly, the presence of Ca, Na, Si, K, Mg, S and P are advantageous for ion-exchange, complexation and chelation of heavy metal ions.

Table 4: XRF analysis of the raw leaf powder of *S. thaipingensis* and the biocarbon

	Concentration (%)	
Formules	Raw leaf powder	Biocarbons
CaO	42.50	47.8
Na_2O	20.80	18.5
SiO_2	13.10	13.4
K_2O	6.27	6.62
MgO	4.21	3.61
SO_3	4.06	2.45
P_2O_5	2.24	1.86
Al_2O_3	1.65	1.16
Fe_2O_3	1.36	1.43
Cl	1.09	0.71
La_2O_3	0.78	0.42
BaO	0.58	0.28
SrO	0.32	0.33
MnO	0.19	0.28
V_2O_5	0.136	nd

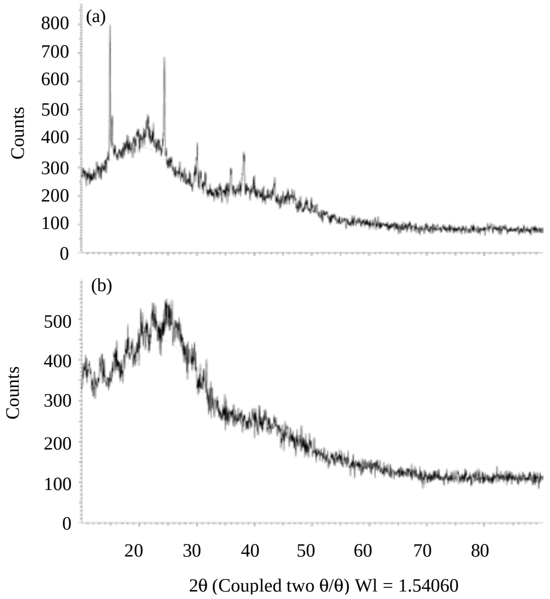

Fig. 1: XRD spectrum of: a) raw *S. thaipingensis* leaf powder. Note the five distinctive peaks at 2θ = 10, 24; 29.5, 36 and 38.5° denoting its intense crystalline structure and b) the biocarbon material produced from the leaf powder by heat treatment. Note the absence of the distinctive peaks observed in the raw leaf powder sample

The XRD profile spectra of the a raw leaf powder and the b biocarbon material is depicted in Fig. 1. Distinct peak

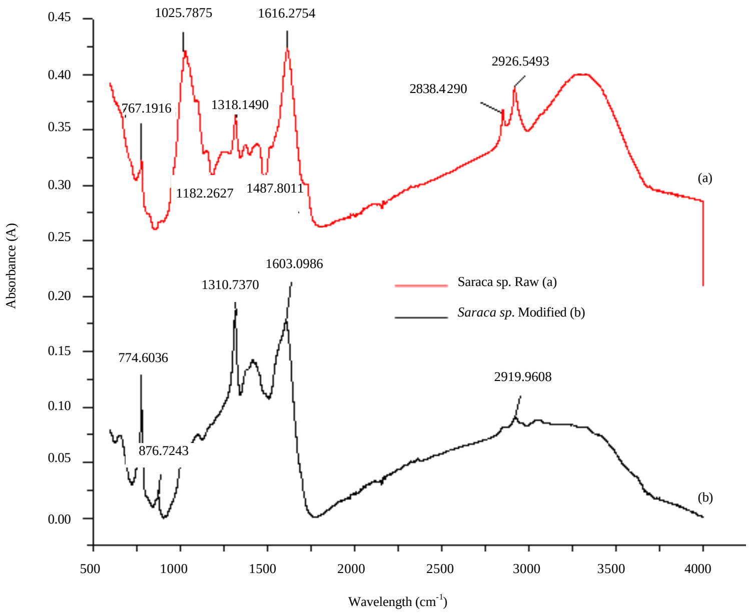

Fig. 2: FTIR spectra of: a) Raw *S. thaipingensis* leaf powder and b) The biocarbon material produced through heat treatment

Table 5: Peak positioning and functional chemical group's assignment of the raw leaf powder and the biocarbon material

Peak No.	Raw powder leaf (cm^{-1})	Biocarbon material (cm^{-1})	Inferences (Nharingo and colleagues)
1	2926	2919	C-H stretch in aliphatic
2	2838	ND	C-H stretch in aliphatic
3	1616	1603	-NH (1° amines), O = C aromatic skeletal stretching
3	1487	ND	C-C(aromatics)
5	1318	1310	C-H asymmetry and symmetry bends
6	1182	ND	C-N (aliphatic amines)
7	1025	ND	C-N (aromatic amines)
8	767	774	C-Cl, C-C stretching

deviations were observed with the samples. A highly amorphous structure would be expected for raw biological material, i.e., leaf powder due to its composition complexity. The five distinct peaks noted with the raw leaf powder were absent in the carbonized sample due to concentration of carbon material. The broad peaks exemplify a more ordered yet not crystalline material. Nevertheless the material was still not homogenous as the leaf powder was only subjected to heat treatment and not chemical activation. The effect of heat may have resulted in the alteration of the pore structure and textural built of the material as can be seen with the biocarbon spectrum.

The FTIR peak positioning scan of the raw leaf zpowder and the heat treated biocarbon material are presented in Fig. 2 and tabulated in Table 5. Variance in terms of number of peaks and stretching positioning are noticeable. The heat treated biocarbon displayed lesser number of peaks as opposed to the precursor material. The relative intensities were also reduced especially those in the range of 800-1500 cm^{-1}. The earlier proximate analysis of the leaf powder showed the presence of up to 75.33% volatile matter, hence evaporation of some of these volatile organic compounds would be reflected in peak reduction. Another aspect would be the evaporation of bound water molecule that would result in peak shifts. Generally plant or agro-based materials are known to harbour many functional chemical groups arising from biochemical compounds such as hemicellulose, lignin, lipids, proteins, sugar, starch, water and hydrocarbons. Heat treatment had affected mainly the-C-H-stretch, -C-C- bonds and -C-N- bonds. The C-H-, -N-H and -C = C-stretch were quite intact with slight shifts in their positioning due to the heat factor. The rich chemical moieties present is ideal for effective removal of Cr(VI) ions.

Figure 3 provides the SEM micrograph of the raw leaf powder. The surface is highly irregular with non-apparent pores. Blocks of mineral deposits are visualized as the lighter components spread over the rough surface.

The SEM micrograph of the newly produced biocarbon material is shown in Fig. 4. Structural porosity formation was evident although irregular throughout the surface area. The hexagon shaped pore-like structure, surface protuberances and folding observed can significantly contribute to increased total surface area which will be of importance for a more effective adsorption process. The plot of pH_i-pH_f against pH_i is

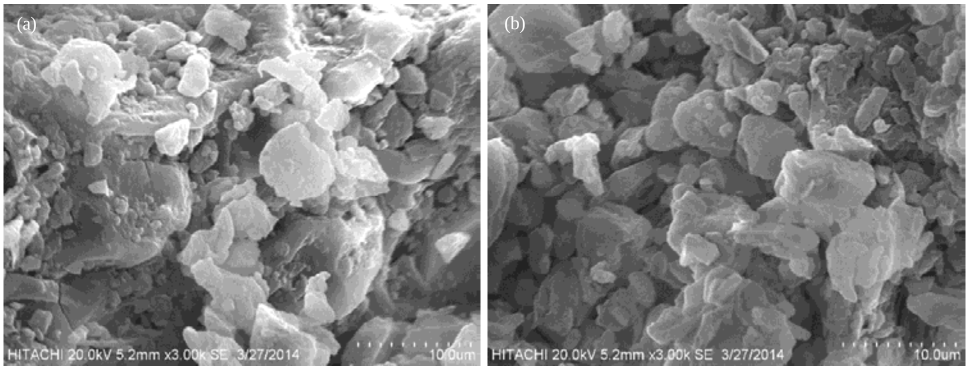

Fig. 3: SEM micrograph of the raw leaf powder of *S. thaipingensis*

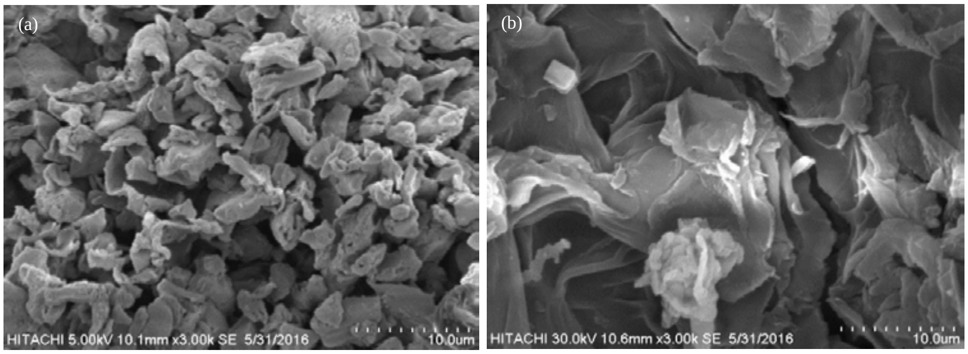

Fig. 4: SEM microgram of the newly prepared *S. thaipingensis* leaf powder-based biocarbon material

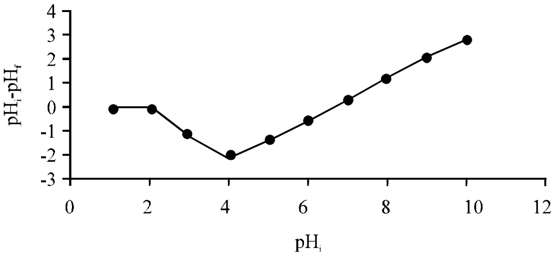

Fig. 5: The plot of pH_i-pH_f against pH_i. (Conditions: agitation speed: 150 rpm; biocarbon dose: 0.1 g; pH: 1-10; contact time: 24 h; room temperature: 25±2°C; volume of NaCl solution: 50 mL; particle size: ≤150 μm)

shown in Fig. 5 and the value of pH_{pzc} of the biocarbon was observed as 6.55 at the intersection. Value of pH_{pzc} represents the pH at which the biocarbon surface acquires net electric charge neutrality. Above this pH_{pzc} value, the biocarbon surface is negatively charged whereas below the pH_{pzc} value, the biocarbon surface is positively charged. Hence, cationic biosorption is favourable above pH_{pzc} value and anionic biosorption is favorable below pH_{pzc} value due to chargeaffinity. Optimal adsorption of mercury (a cation) was reported at pH 6 and the pH_{pzc} of Phragmites karka was 4.5 (Raza *et al*., 2015). Similar trend of the plot have been reported and the pH_{pzc} value of activated carbons prepared from the leaves of Ricinus communis was 6.04 (Makeswari and Santhi, 2013), Punica granatum peel was 6.53 (Guzel *et al*., 2012) and Tamarindus indica seed was 6 (Agarwal *et al*., 2006).

Effect of contact time towards Cr(VI) removal: Figure 6 shows the percentage removal of Cr(VI) at 100 mg/L carried out by varying the time of biocarbon contact with Cr(VI) solution from 30-300 min. The highest mean percentage removal of Cr(VI) was recorded at 300 min. The increase in contact time raised the percentage removal of Cr(VI) from 33.74-92.90%. This was significantly ($p<0.05$) higher compared to the readings at 30, 60, 120 and 180 min. This would be due to the prolonged exposure of the biocarbon material to the Cr(VI) ions in the solution which would allow for increased contact collision to occur. The difference in percentage removal between 240 and 300 min was insignificant indicating saturation in surface coverage and active sites reaching an e quilibrium state (Sinha *et al*., 2013; Raza *et al*., 2015). For subsequent experiments, the contact time of 180 and 240 min (3 and 4 h) were opted.

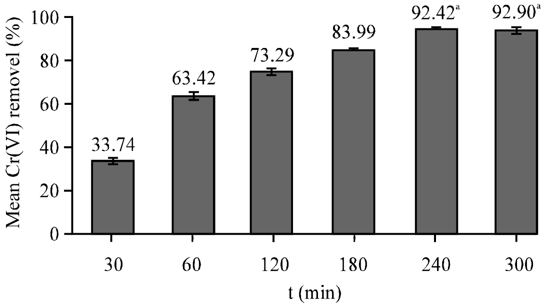

Fig. 6: Mean percentgae removal of Cr(VI) against contact time (min). Readings are mean±SE of mean (n = 3); (Conditions: agitation speed: 250 rpm; biocarbon dose: 0.125 g; pH: 2; room temperature: 25±2°C; volume of Cr(VI) solution: 25 mL; particle size: 150 μm; initial concentration of Cr(VI): 103.44 mg/L); ^{a}significant at $\alpha = 0.05$

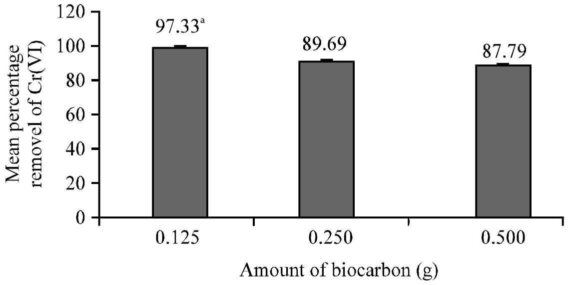

Fig. 7: Mean percentage removal of Cr(VI) against amount of biocarbon (g); readings are mean±SE of mean (n = 3); (Conditions: agitation speed: 250 rpm; biocarbon dose: 0.125, 0.25 and 0.5 g; contact time: 240 min; pH: 2; room temperature: 25±2°C; volume of Cr(VI) solution: 25 mL; particle size: ≤150 μm; initial concentration of Cr(VI): 97.83 mg/L); ^{a}significant at $\alpha = 0.05$

Effect of biocarbon dosage: The effect of biocarbon dosage towards Cr(VI) removal was carried out by varying the amount of biocarbon used from 0.125-0.500 g. The results are shown in Fig. 7. The higher biocarbon dosage from 0.125-0.500 g showed decrease in percentage removal of Cr(VI) from 97.33-87.79%. The highest mean percentage removal of Cr(VI) was obtained at 0.125 g (97.33 %) which was significantly ($p<0.05$) higher compared to using 0.25 and 0.5 g biocarbon dosage. Hence, 0.125 g of biocarbon dosage was chosen for the following experiments. High adsorption capacity observed at 0.125 g may be due to the sufficient number of active binding sites on the biocarbon available for Cr(VI) adsorption. Decrease in percentage removal at higher dosage could be due to the aggregation of the biocarbon material in the solution thus decreasing the effective number of active sites accessible for Cr(VI) ions to interact. Similar outcome of dosage effect was observed in studies of Cr(VI) removal (Vinodhini and Das, 2009; Mohanty *et al*., 2014); Cu(II) removal (Ghosh *et al*., 2015), Zn removal (Rajoriya and Kaur, 2014) and Mn(II) removal.

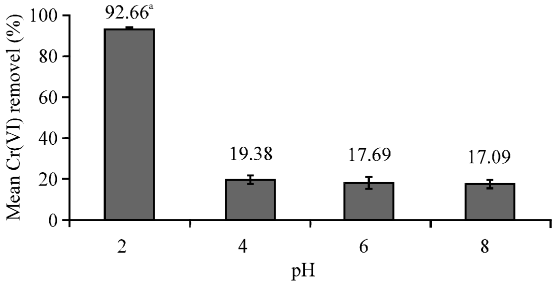

Fig. 8: Mean percentage removal of Cr(VI) against pH. Readings are mean±SE of mean (n = 3); (Conditions: agitation speed: 250 rpm; biocarbon dose: 0.125 g; pH: 2, 4, 6 and 8; contact time: 240 min; room temperature: 25±2°C; volume of Cr(VI) solution: 25 mL; particle size: 150 μm; initial concentration of Cr(VI): 103.44 mg/L); ^{a}significant at $\alpha = 0.05$

Effect of initial pH: The experiment to study the effect of pH towards Cr(VI) removal was carried out by varying the initial pH of Cr(VI) solution from pH 2-H 8. The results are shown in Fig. 8. The highest mean percentage removal of Cr(VI) was obtained at pH 2 (92.66%). This was significantly ($p<0.05$) higher when compared to percentage removal at pH 4, 6 and 8. This would be due to the strong electrostatic attraction between the positively charged biocarbon and the negatively charged chromate, dichromate and hydrogen chromate ions (Sinha *et al*., 2013; Mohanty *et al*., 2014).

The high occurrence of H^+ at low pH can induce the protonation of functional chemical groups such as carboxyl and amines found on the biocarbon material. This would result in strong attraction between the oxyanion of Cr(VI) and the positively charged of biosorbent. So at lower pH this condition will favour higher uptake and removal of Cr(VI) ions. As can be seen from Fig. 9, raising the pH from 2-8 showed decrease in the percentage removal of Cr(VI) from 92.66-17.09%. The sharp decline observed at both pH 4 and 6 might be attributed to the diminishing electrostatic attraction between the gradually more positive biocarbon and the negatively charged chromate, dichromate and hydrogen chromate ions, since amount of H^+ decreases with

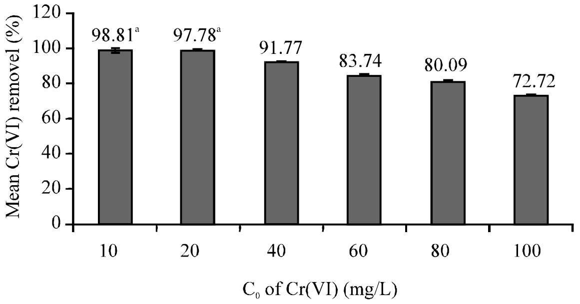

Fig. 9: Mean percentage removal of Cr(VI) against initial concentration of Cr(VI). Readings are mean±SE mean (n = 3); (Conditions: agitation speed: 250 rpm; concentration of Cr(VI): 10, 20, 40, 60, 80 and 100 mg/L; biocarbon dose: 0.125 g; pH: 2; contact time: 180 min; room temperature: 25±2°C; volume of Cr(VI) solution: 25 mL; particle size: 150 μm); [a]significant at $\alpha = 0.05$

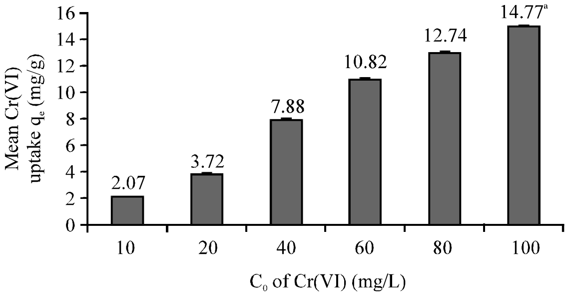

Fig. 10: Mean Cr(VI) uptake, qe (mg/g) against initial concentration of Cr(VI). Readings are mean±SE of mean (n = 3); (Conditions: agitation speed: 250 rpm; concentration of Cr(VI); 10, 20, 40, 60, 80 and 100 mg/L; biocarbon dose: 0.125 g; pH: 2; contact time: 180 min; room temperature: 25±2°C; volume of Cr(VI) solution: 25 mL; particle size: 150 μm]; [a]significant at $\alpha = 0.05$

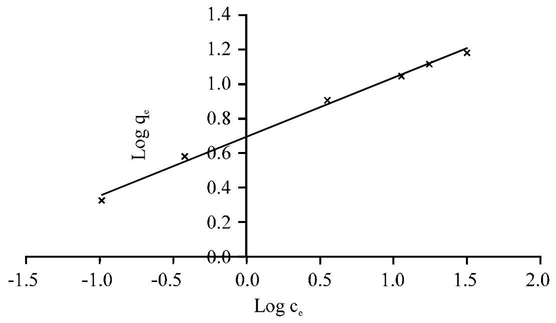

Fig. 11: Freundlich isotherm (linear form) for removal of Cr(VI) by heat-treated biocarbon (Conditions: agitation speed: 250 rpm; biocarbon dose: 0.125 g; pH: 2; contact time: 180 min; room temperature: 25±2°C; volume of Cr(VI) solution: 25 mL; particle size: ≤150 μm)

increasing pH (Gupta and Mote, 2014). Hence, deprotonation of functional groups on the biocarbon will start to occur. At the same time, there will be build-up in the concentration of negatively charged hydroxyl ions in the aqueous solution. This situation will hinder further biosorption process leading to lower Cr(VI) removal.

The lowest percentage removal was observed at pH 8 because of the intense competition between the negatively charged chromate, dichromate and hydrogen chromate ions and the OH^- ions. Other researchers working with Cr also reported pH 2 as optimum for the removal of Cr(VI) with their adsorbents systems (Agarwal *et al.*, 2000; Sen and Dastidar, 2010; Gupta and Mote, 2014). The optimum pH of pH 2 is lower than the value of pH_{pzc} determined earlier hence adsorption of anionic Cr(VI) is favoured by the positively charged biocarbon. Cationic adsorption would be expected to have an optimum pH higher than $pH_{pzc} = 6.55$.

Effect of initial concentration: The effect of varying concentration of Cr(VI) solutions in the range of 10-100 mg/L towards Cr(VI) removal and uptake are shown in Fig. 9 and 10, respectively. The highest mean percentage removal was observed at 10 mg/L (98.81%) and the highest uptake at 100 mg/L (14.77 mg/g), respectively after 180 min. The percentage removal of Cr(VI) at 10 and 20 mg/L was significantly ($p<0.05$) higher compared to 40, 60, 80 and 100 mg/L. At lower Cr(VI) concentration, the ratio of available unadsorbed Cr(VI) ions to active sites on the biocarbon is small and hence the adsorption is independent of Cr(VI) concentrations (Makeswari and Santhi, 2013). At higher Cr(VI) concentration, the ratio of active sites available on biocarbon become fewer as the amount of biocarbon is constant, thus adsorption becomes dependent upon Cr(VI) concentrations. This results in lower removal capability (Sinha *et al.*, 2013; Gupta and Mote, 2014). The uptake of Cr(VI) at 100 mg/L on the other hand was significantly ($p<0.05$) higher compared to other Cr(VI) concentrations as more Cr(VI) ion are concentrated per unit mass of biocarbon. Cr(VI) uptake increases with the increase in Cr(VI) concentration.

Adsorption isotherms: The best isotherm model was based on correlation coefficient (R^2) goodness of fit. For $R^2<0.9$, the isotherm fit is deemed poor whereas if $0.9\leq R^2\leq 0.99$, it shows that the model fits well with the experiment data (Okeola and Odebunmi, 2010). The overall tabulation of model fit is given in Table 6 and the best plot shown in Fig. 11. The best model to describe Cr(VI)

Table 6: Isotherm parameters for the removal of Cr(VI) by the biocarbon material

	Parameters				
Isotherm types	q_{max} (mg/g)	b (L/mg)	R^2	R_L	Equation
Langmuir-1	15.29	0.43	0.9814	0.427	y = 0.0654x+0.1515
Langmuir-2	9.90	2.63	0.9398	0.079	y = 0.0384x+0.1010
Langmuir-3	12.81	1.42	0.7341	0.142	y = -1.4165x+18.145
Freundlich	-	-	-	-	y = 0.3514x+0.6808

n = 2.85; K_f = 4.80; R^2 = 0.9963

removal and uptake by the biocarbon material is by the Freundlich model (R^2 = 0.9963) as opposed to Langmuir models (R^2 range: 0.7341-0.9814; plots not shown). The process constant, n value of 2.85 indicates a favourable biosorption process. The maximum Cr(VI) uptake at 100 mg/L was calculated as 24.15 mg/g by using the following equation $K_f = q_m/C_o^{1/n}$. Moreover, the determination of R_L constant, where $R \underset{L}{>} 1$, represents unfavourable biosorption; $R_L = 1$, represents linear biosorption; $R_L = 0$, represents irreversible biosorption (Singanan and Peters, 2013). The R_L value determined for Cr(VI) adsorption with the biocarbon indicates a favourable process as $0<R_L<1$. Lower value of R_L means that there is a strong interaction between the adsorbate, Cr(VI) and the adsorbent, biocarbon (Singanan and Peters, 2013). Equation for R_L is given as:

$$R_L = 1/[1 + bC_o]$$

where, C_o is the initial concentration of Cr(VI) (Kumar and Tamilarasan, 2013).

Adsorption kinetics and mechanism: In order to examine the process behaviour, rate controlling steps and limiting factors in the removal of Cr(VI), the following models (Gupta and Mote, 2014) were applied. The linear pseudo-first order model expressed in the form of:

$$\log(q_e - q_t) = \log q_e - K_1/2.303t$$

Where:

q_e and q_t = The amount of ions adsorbed (mg/g) at equilibrium and at any other time

t (min) and K_1 = The rate constant (min^{-1})

The linear pseudo-second order model expressed in the form of: $t/q_t = [1/K_2q_e^2+1/q_e]t$ where k_2 is the rate constant (g/mg/min/); $h = K_2q_e^2$. The intra-particle diffusion model expressed in the form of: $q_t = K_{id}t^{1/2}+C$ where K_{id} is the intra-particle diffusion rate constant ($mg.g^{-1}.h^{1/2}$). All the kinetic constants shown in Table 7 were determined from the intercept and slope of the respective model's linearized plots (Fig. 12-14). The better fit observed through the pseudo-second order kinetic model suggest that adsorption is likely governed by chemical reaction or known as chemisorption.

Table 7: Adsorption kinetic constants for the removal of Cr(VI) by the biocarbon material

Varibles	Values
Pseudo-first order	
K_1 (min^{-1})	0.029
R^2	0.9006
Pseudo-second order	
K_1 (g/mg/min)	9.047×10^{-4}
R^2	0.9946
Intra-particle diffusion	
K_{id} (($mg.g^{-1}.h^{1/2}$)	0.6904
C	7.8417
R^2	0.9683

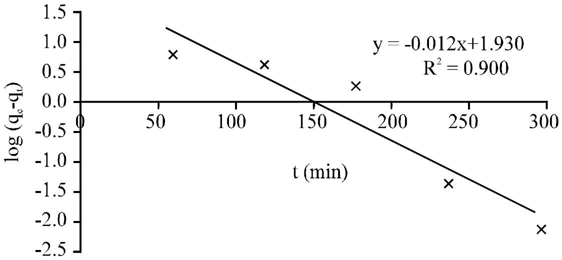

Fig. 12: The pseudo-first order kinetic model plot of Cr(VI) removal by the biocarbon material

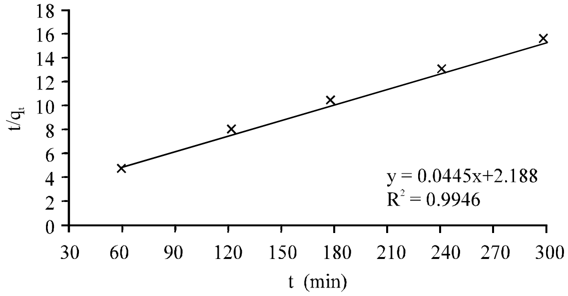

Fig. 13: The pseudo-second order kinetic model plot of Cr(VI) removal by the biocarbon material

The adsorbate will bind to the adsorbent surface by chemical interaction resulting from the attracting force between the adsorbed component and the solid surface. In addition, due to the strength of the force, substances that chemisorbed on the solid surface are hardly removed

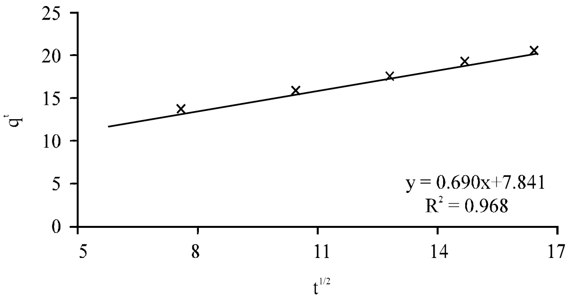

Fig. 14: The intra-particle diffusion rate model plot of Cr(VI) removal by the biocarbon material

and the chemisorption occurs as a monolayer (Gupta and Mote, 2014). The intercept of the intra-particle diffusion model shows the boundary layer effect. A linear plot passing through the origin would indicate that intra-particle diffusion is the rate-limiting step. However, in the removal action of Cr(VI) by the biocarbon, surface sorption is postulated to be the dominant mechanism and intra-particle diffusion is not the rate controlling step. Further work is being carried out to investigate chemical changes to the adsorbed Cr and its interaction with the Cr ions in the solution at any time. This will be followed by continuous Cr(VI) removal by column studies.

CONCLUSION

There are many advantages of using a low cost bioadsorbent. These include better or improved efficiency in removing toxic heavy metal ions with options for bioadsorbent recovery and regeneration, no generation of chemical sludge and able to cater for a wider range of target pollutants (Rao and Prabhakar, 2011; Ghosh *et al.*, 2015). The bioadsorbent can also be customized to acquire high surface area to volume ratio as opposed to conventional tools used in filtration. Importantly, the low cost bioadsorbent can become a cost-effective and cost saving alternative as conventional methods usually consume high energy and high amount of chemicals (Sen and Dastidar, 2010) and are less practical when the toxic heavy metal ions are present at low concentration. This would make the overall process more expensive. Hence, bioadsorbent originating from plant refuse or waste that exhibit good metal binding capacity potential will be the more suitable choice. A large number of plant refuses are being tested for use in metal remediation and recovery. But, to improve the competitiveness of industrial processing operations, it is necessary that the economic aspects of biosorbent development technology be taken into account as well, i.e., the plant refuse must be cheap, largely available, capable of reducing heavy metals under a wide range of pH, temperature and has rapid kinetic adsorption and desorption traits with significant pollutant removal capability. The newly produced biocarbon material from the leaf litter of *S. thaipingensis* by means of heat treatment had been successfully tested to remove Cr(VI) ions from aqueous solution. Characterization study findings concurred well with the adsorption behaviour of the biocarbon material towards Cr(VI). The process is very much influenced by surface chemistry and solution pH which affects surface charge as well as Cr(VI) ion speciation. An increase in the fixed carbon content (from 47.62-58.35%) and reduced ash content were evident effect of heat treatment onto the leaf powder biomass. Both characteristics are preferred in the production of carbonized bioadsorbents. The effects of contact time, biocarbon dosage, initial pH and initial Cr(VI) concentration towards the removal of Cr(VI) by the heat-treated biocarbon had been investigated. Based on the outcome of this research, the following can be concluded. The percentage removal of Cr(VI) significantly increased from 33.74-92.90% with increasing contact time over a period of 30-300 min. An increase in biocarbon dosage from 0.125 -0.500 g showed declining Cr(VI) removal from 97.33-87.79%. Initial solution pH greatly affects Cr(VI) removal. An increase of pH from 2-8 resulted in lower percentage removal from 92.66-17.09%. Value of pH_{pzc} was found to be 6.55. This value showed that biosorption of Cr(VI) is favourable below pH of 6.55. Increasing Cr(VI) concentration from 10 mg/L-100 mg/L showed a decrease in percenatge removal from 98.81-72.72% but saw an increase in Cr(VI) uptake from 2.07-14.77 mg/g biocarbon. Adsorption followed the Freundlich model ($K_f = 4.80$, $n = 2.85$, $R^2 = 0.9963$) and pseudo-second order kinetics ($R^2 = 0.9946$) implying a multilayer surface chemisorption accompanied by interactions between the adsorbed Cr on the biocarbon surface and Cr ions in the solution. Overall characterization supported the above results as SEM examination revealed pore-like structures that can adsorb Cr in the biocarbon and the rich and diverse chemical functional groups (-C-H-, -C-C-, -C = C-, -C-N-, -N-H-) and oxides (Ca, Na, Si) that can facilitate adsorption were observed through FTIR and XRF analyses.

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