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Green Pea Pod Biochar as a Low-Cost Adsorbent: An Alternative Approach for the Removal of Cr (VI) from Aqueous Solution

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ABSTRACT

In the present study, Pisum Sativum (Green pea) pod were converted to biochar with slow pyrolysis at 450°C and utilized for hexavalent chromium removal from aqueous solution. Batch adsorption studies were carried out to evaluate the effect of initial pH, biochar dosage, initial Cr (VI) concentration and contact time. The highest removal of Cr (VI) was achieved at pH 2.0 using a 4 gm/L of biochar dose with 10 mg/L of Cr (VI) concentration. The Langmuir isotherm model was fitted best with maximum uptake capacity of 33.33 mg/g. FTIR analysis was carried out for GPPB450 before and after Cr (VI) adsorption to understand the role of functional moieties.

Key words: *Biochar, Adsorption isotherm, Hexavalent chromium, Pea pod*

INTRODUCTION

Biochar is a carbon rich, fine grained and porous solid product produced from thermal degradation of organic matter with aromatic surfaces. It is an intermediate solid residue, which is formed in the pyrolysis of most biomass[1]. It is created for thermal stabilization of organic matter for safe and potentially beneficial storage in soil. The primary objective of the biochar production is long-term carbon storage, rather than creation of feedstock for processing industries or fuels such as charcoal, coke and activated carbon[2].

Biochar can be prepared from different organic feed stocks such as wood and biomass crops[3], agricultural byproducts[4], food industry residues[5], house-hold organic wastes and also from different other wastes such as waste plastic, sewage sludge, bones and feathers of animals and birds etc[6]. According to the International Biochar Initiative Organization, it is estimated that by the year 2050 about 80% of all crop and forestry residues may be converted to biochar and energy[7].

Different kind of thermochemical process such as pyrolysis, hydrothermal carbonization, gasification are generally used for the biochar production[8]. At low temperature and slow heating rate process, high biochar production can be gained from the pyrolysis process[9].

Biochar is a promising material for climate change mitigation and adaptation, as it can sequester atmospheric carbon while improving the quality of soil where it is stored [10]. It is analyzed that the global potential for sustainable global biochar deployment, with results showing that net emissions of GHGs could be reduced by as much as 1.8 Gt CO_2–C equivalent per year (i.e., 12% of current anthropogenic emissions)[11].

Heavy metals pose a risk to public health because of their toxic and non-biodegradable nature and widespread occurrence in natural and human-altered environments. They are mainly introduced into the environment from point sources such as discharges from mining, metal plating, battery, and paper industries [12]. Chromium is one of the toxic heavy metal which is widely detected in chromate manufacturing, leather tanning, wood preservation, and electroplating industries[13]. Chromium existing in hexavalent (Cr (VI)) and trivalent (Cr (III)) forms generally. Cr (VI) is much more soluble and mobile in aqueous solutions than Cr (III), and due to its carcinogenic, mutagenic and teratogenic effects on biological chain it is very necessary to develop methods for effectively removal of harmful Cr (VI) from water[14].

Many techniques are used to reduce the Cr (VI) concentration in the environment, such as sedimentation, chemical precipitation, membrane separation, ion exchange, ultrafiltration, and adsorption[15]. The bioavailability, reactivity, and mobility of contaminants are well controlled by adsorption[16]. Therefore, it is necessary to prepare a low-cost adsorbent with a high adsorption capacity. In many previous studies the use of low cost adsorbents showed higher potential for Cr removal from wastewaters[17-20]. Biochars possess strong affinity for non-polar substances such as PAHs, dioxins, furans, and other compounds and poses high surface-to-volume ratio, so, biochar can be used as a potential sorbent for organic and inorganic pollutants [21,22,23]

Pisum Sativum (Green pea) pod is abundantly available organic residual biomass from house hold to large scale food processing industries. This residual biomass has no utilization besides animal fodder, occasionally. Dumping of residues to landfill sites increase the green house gas (GHG) emission. Abundance of pea pod biomass can be a potential source for biochar production and the produced biochar can be utilized for various aspects of environmental management. In this context, the present study investigated the use of green pea pod biomass waste as the feedstock for biochar production and to study the potential of biochar for remediation of hexavalent chromium from aqueous solution. Previous study on pea pod derived biochar was done for the characterization purpose [24].

MATERIAL AND METHODS
Biochar preparation
Green Pea Pod (GPP) was collected from the local market of Ghaziabad city Uttar Pradesh. Sample was washed thoroughly with distilled water and air dried at 60°C till the moisture content reached up to < 10%. After drying, sample was grounded and sieved to < 1mm then placed into a horizontal tube furnace for carbonization under continuous N_2 flow. The temperature of the furnace was raised to 450°C with a constant heating rate of 5°C min^{-1} and held for 60 min followed by cooling to room temperature inside the furnace. The developed biochar was stored in an air tight plastic container and hereafter referred as GPPB450.

FTIR characterization of biochar
Fourier Transform Infrared Spectrophotometer (FTIR) (Cary 630, Agilent Technologies) was used to identify the surface functional groups in biochar. The spectra were recorded over the 4000-400 cm^{-1} wave range. To understand the Cr (VI) removal mechanism the FTIR spectra was also measured after the adsorption. A total 32 scans with 4 cm^{-1} resolution were taken.

Batch adsorption studies
Preparation and analysis of Cr(VI) solution
The stock solution of 1000 mg/L of Cr (VI) was prepared by dissolving 2.892 gm of $K_2Cr_2O_7$ (SRL, India) into 1000 ml of deionized water. All the subsequent solutions were prepared by appropriate dilution of the stock solution. The remaining concentration of

Cr (VI) ions were analyzed using a UV-vis spectrophotometer (SL-159, ELICO). The 1,5-diphenylcarbazide (DPC) method was used to detect the remaining concentration of Cr (VI). The violet- purple colored complex was formed after the reaction of Cr (VI) and DPC. The absorbance of resulting complex was measured at 540 nm after 10 min of reaction. All the experiments were carried out in triplicates.

Batch adsorption experiment

Batch adsorption studies were carried out at different pH (2-7), biochar dosages (0.5 – 5 g/L), initial Cr (VI) concentrations (20-200 g/L) and contact time till 300 min. All the experiments were carried out at 30°C in 50 ml of Erlenmeyer flask containing 20 ml of Cr (VI) solution of appropriate dilution. A thermostat orbital incubator shaker (INNOVA 42, Thermo Fisher) with a constant rpm of 200 was used for all the experiments. All the flasks were sealed and the reaction was preceded under dark conditions. After completion of experiments, suspensions were filtered and filtrate was used for Cr (VI) determination. The amount of sorbed Cr (VI) Qe was calculated in mg/g according to,

$$q_e = (C_0 - C_e) * V / m \qquad (1)$$

Percentage removal of Cr (VI) was calculated according to,

$$\% \text{ Removal} = [(C_0 - C_e) / C_0] * 100 \qquad (2)$$

Where C_o and C_e are the initial and equilibrium Cr (VI) concentrations respectively in mg/L in the aqueous solution, m is the mass of biochar used in gm and V (L) is the volume of the solution.

Adsorption Isotherm

Langmuir, Freundlich and Temkin isotherm models were selected to explain Cr (VI)-GPPB450 interaction.

Langmuir Isotherm

This model is applicable when a monolayer of adsorbate is formed at the surface of adsorbent, and it remains constant even at higher adsorbate concentrations. The model can be presented by the equation [25]

$$Ce/Q_e = (1/q_m K_L) + (Ce/Q_m) \qquad (3)$$

Where Ce is the equilibrium metal ion concentration in the solution (mg/L), Q_e is the equilibrium metal ion concentration on the adsorbate (mg/gm), Q_m is the maximum adsorption capacity of the adsorbent (mg/gm) and K_L is the Langmuir adsorption constant (L/mg). Values of q_m and K_L are predicted respectively from slop and intercept of the plot between Ce/Q_e vs. Ce.

Langmuir isotherm was also expressed with a dimension less constant known as separation factor R_L.

$$R_L = 1/(1 + C_0 * K_L)$$

If $R_L > 1$ unfavorable; $R_L = 1$ linear; $R_L < 1$ favorable. R_L predicts whether the adsorption process is favorable or not.

Freundlich Isotherm

The Freundlich adsorption isotherm assumes that adsorption takes place on heterogeneous surfaces, can be expressed as

$$\log qe = \log K_f + n \log Ce \qquad (4)$$

Where K_f is the Freundlich constant related to the adsorption capacity and n is an empirical parameter related to the adsorption intensity

Temkin isotherm

Temkin isotherm model can be represented as

$$Qe = (RT/b) \ln K_T + (RT/b) \ln Ce \qquad (5)$$

Where B = RT/b,
K_T is the equilibrium binding constant (L/mg), R is the gas constant (8.314 J/mol /K), T is the temperature (K), b is the Temkin isotherm constant, B is the constant related to heat of sorption (J/mol).

Quality Control and Statistical Analysis

All the reagents used in this study were AR grade only. All the experiments were performed in triplicates. The adsorption of Cr (VI) was calculated with respect to the values in the controls. All the analysis was done with the help of Microsoft Excel software (windows 7).

RESULTS AND DISCUSSION
Batch sorption study
Effect of initial solution pH

The pH of the aqueous solution governs the speciation of the metal and the properties of the surface. For concentration lower than 500 mg/L of Cr (VI), the predominant species are $HCrO^{-4}$ and CrO_4^{2-} anions [26]. At solution pH values between 2.0 and 6.0, Cr (VI) ions are probably in solution as $HCrO^{4-}$ and $Cr_2O_7^{2-}$ species[27]. Fig. 1 illustrated the effect of pH onto the Cr (VI) removal capacity of

GPPB450. It is clear that the Cr (VI) removal is highly dependent on pH and the maximum removal efficiency (95%) was achieved at pH 2. Low pH leads to an increase in H^+ ion concentration in the system and the surface of the GPPB450 may acquires positive charge by adsorbing H^+ ions which leads to protonation of its functional groups. As the GPPB450 surface is positively charged at low pH, a significantly strong electrostatic attraction appears between positively charged sites and negatively charged chromate ions [28]. At higher pH values the concentration of H^+ ions decreases and the concentration of OH^- ions increases in the solution, and the sorbent surface charge become negative, leads to decrease in the chromium species retention [26]. Further, the lower adsorption of the Cr (VI) in alkaline medium may also be due to the competition between excess OH^- ions and the anionic chromium species[29,30].

The pH of the Cr (VI) solution was measured after adsorption and for clear understanding purpose it is taken as the final pH in presence of Cr (VI). The initial pH of Cr (VI) solution was plotted against the final pH of solution (Fig. 1). It is clear from the figure that as the initial pH of the solution increases the equilibrium pH also increases, it may be due to the deprotonation of the adsorbent functional groups which release OH^- ions resulting in the increase of the final pH.

Effect of the adsorbent dosage
In order to investigate the effect of biochar dose on the Cr (VI) sorption, different amounts of GPPB450 (0.5 to 5 mg/L) was suspended in 20 ml of 10 mg/L of Cr (VI) solution with pH 2. For metal removal amount of adsorbent dosage is an important factor, as it determines the sorbent-sorbet equilibrium of the system. The effect of biochar dosage onto the Cr (VI) adsorption is depicted in Fig. 2. The removal rate increases from 57% to 96% as the adsorbent dose increased from 0.5 gm/L to 4 gm/L and remain constant for 5 gm/L. The removal of Cr (VI) increases up to a certain limit (4 mg/L) and remains almost constant thereafter. Therefore, the dose of 4 gm/L was selected for the further experiments. An

increase in adsorption with the adsorbent dose can be attributed to increase surface area and the availability of more adsorption sites [31]. In contrast, the amount adsorbed for unit mass of biochar decreases as the dose of biochar increases (Fig. 2). At low adsorbent dose all active site of the biochar are fully exposed and occupied by the Cr (VI) which is in excess, saturating the surface and yielding the higher Qe, while the decrease in unit adsorption with increasing dose of adsorbent is basically due to the adsorption sites remain unsaturated during the adsorption process [26,32].

Effect of contact time
The effect of contact time on the removal of Cr (VI) by GPPB450 at initial metal concentrations of 5, 10 and 15 mg/L, at pH 2 and a constant adsorbent dose is shown in Fig. 3. The percentage removal of Cr (VI) by GPPB450 was 99%, 95%, and 90% respectively for each initial Cr (VI) concentrations. It is observed that the metal uptake is rapid initially and thereafter proceeds at a slower rate and finally attained saturation, which was reached at nearly 180 min. Further increase in contact time did not show any significant uptake. This kind of behavior during adsorption may be attributed to the fact, that initially, all active sited of biochar was available which were filled in due time. After that only few active sites were available for the uptake of Cr (VI) which decreases the Cr (VI) retention [30].

Effect of initial Cr (VI) concentration
The effect of initial Cr (VI) concentration on the adsorption process was investigated on a range of different initial Cr (VI) concentrations, while other parameters were kept constant (Fig. 4). It was observed that as the initial Cr (VI) concentration increases, the removal percentage decreases from 91% to 41%. It may be due to the number of active sites may remain constant as the dose of the biochar was constant, while the concentration of Cr (VI) was increased. At such higher concentration of Cr (VI) there may not enough active sites remain to remove the total Cr (VI) present in the solution. On the other hand, as the initial Cr (VI) concentration increased, the

adsorption capacity of biochar increased from 5.16 to 31.64 mg/g. The higher availability of Cr (VI) ions in the solution may increase the rate of mass transfer from the solution to the solid adsorbent which may cause the increase of adsorption capacity of biochar [33].

Adsorption isotherm models

The experimental results shown in Fig. 4 were fitted to the Langmuir, Freundlich and Temkin adsorption isotherm models (Fig. 5 A-C). All the calculated parameters for the above isotherm models were listed in table 1. The results shows that the experimental data best fitted with Langmuir isotherm with higher correlation coefficient (R^2 0.947) than others. Also, the calculated Qm value is near to the experimental Qe (Table 1). The results indicate that the adsorption of Cr (VI) onto GPPB450 is a monolayer adsorption process with limited number of active sites. The calculated Qm value 33.33 mg/g suggested

comparable uptake capacity with other low cost adsorbents (Table 2)

FTIR Analysis

The FTIR spectrum of GPPB450 before and after adsorption is shown in Fig. 6. Changes in 3500 – 3200 cm^{-1} were observed corresponding to –OH stretching [34]. Medium peaks at 2928 cm^{-1} and 2854 cm^{-1} were observed after adsorption referred to –CH stretching of symmetric and asymmetric aliphatic [30]. Shift was observed from 1564 cm^{-1} to 1596 cm^{-1} after Cr (VI) adsorption which is corresponding to the –CH stretching of the lignin and cellulose [35]. Disappearance of the peak at 1317 cm^{-1}, 1027 cm^{-1}, 776 cm^{-1} and 759 cm^{-1} while new peak at 811 cm^{-1} was observed. Significant changes in the functional groups were observed demonstrating the active contribution of functional groups into chromium adsorption.

Table 1: Isotherm parameters for adsorption of Cr (VI) on GPPB450

Isotherm model	Parameters					
Langmuir Isotherm	Q_m (mg/g)	33.33	K_L (L/mg)	0.04	R^2	0.947
	R_L	0.003 – 0.048				
Freundlich isotherm	K_f (mg/g)	1.98	n (g/l)	0.347	R^2	0.894
Temkin isotherm	K_T (L/g)	1.2001	B (mol^{-1})	5.109	R^2	0.881

Table 2. Adsorption capacity of other low cost adsorbents compared with GPPB450

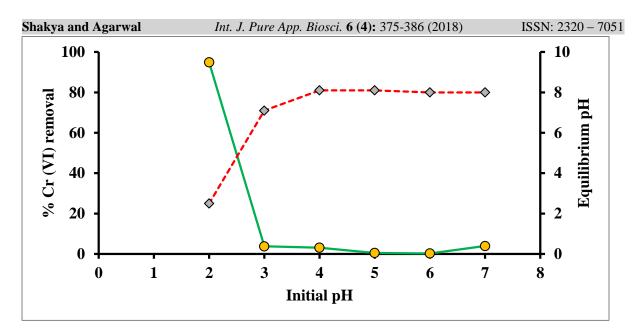| Biochar	Qm (mg/g)	Reference
Melia azedarach wood biochar (magnetic)	25.27	[36]
Oak wood biochar	3.031	[37]
Ferticompost	6.25	[26]
Rice straw	3.15	[38]
Corn-bran residue biochar	39.75	[39]

Fig. 1: Effect of initial pH of the solution on the removal of Cr (VI) from aqueous solution using GPPB450
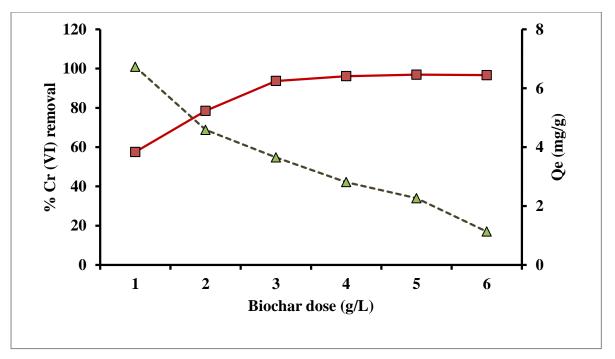

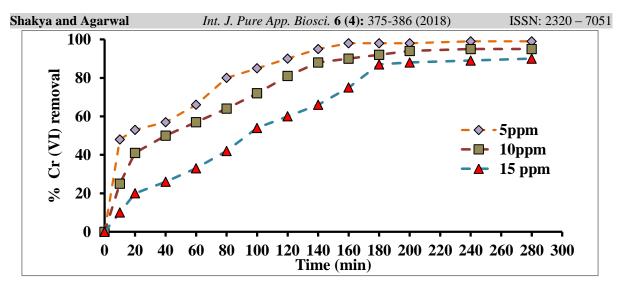**Fig. 2: Effect of GPPB450 dosage on the adsorption of Cr (VI)**

Fig. 3: Effect of contact time on the Cr (VI) removal from aqueous solution by GPPB450
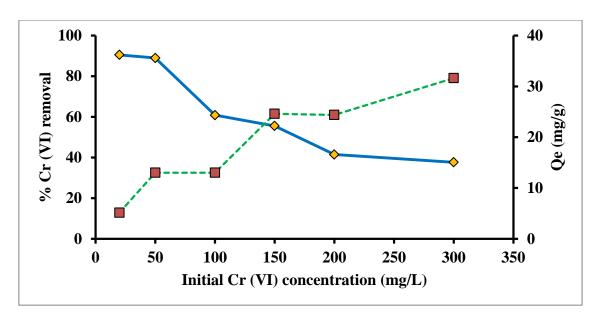

Fig. 4: Effect of initial Cr (VI) concentration on the adsorption of Cr (VI) from aqueous solution with GPPB450
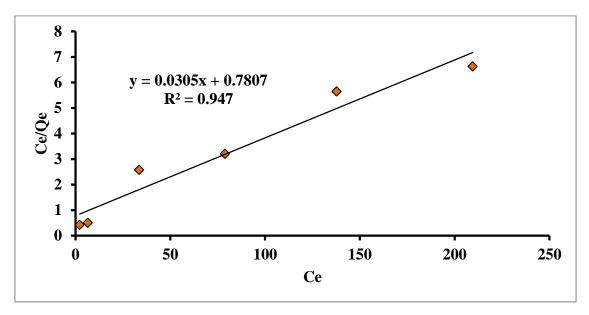

$$y = 0.0305x + 0.7807$$
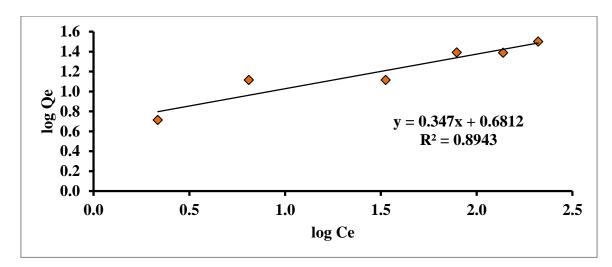$$R^2 = 0.947$$

Fig. 5 A. Langmuir isotherm plot

Fig. 5 B. Freundlich isotherm plot

Fig. 5 C. Temkin isotherm plot

Wavenumber (cm^{-1})

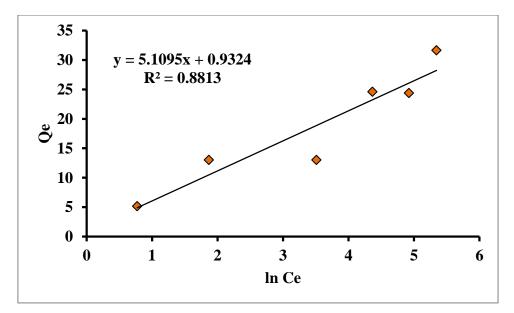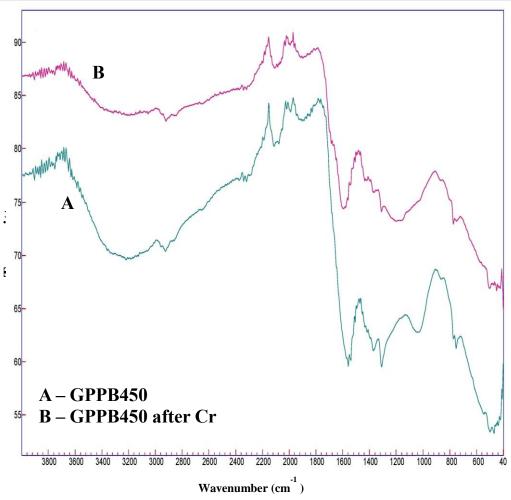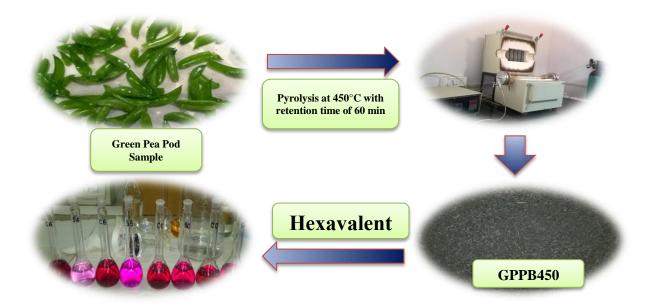**Fig. 6: FTIR spectral analysis of GPPB450 (A) before and (B) after Cr (VI) adsorption**

CONCLUSION

The present study explored the use of green pea pod a residual biomass from food industry. It is observed that the adsorption of Cr (VI) was strongly dependent on pH. Moreover, the Cr (VI) removal rate was strongly dependent on pH, initial Cr (VI) concentration, contact time and adsorbent dose. Highest removal was achieved at pH 2. The Langmuir isotherm was best fitted with the experimental data which shows monolayer adsorption mechanism may takes place for Cr (VI) adsorption with GPPB450. The maximum uptake capacity of GPPB450 was found to be 33.33 mg/g. FTIR data suggested rearrangement of surface functional groups after the adsorption, which indicates the strong involvement of surface functionality in adsorption process.

REFERENCES

1 Ghani, W. A. W. A. K., Biochar production from waste rubber-wood-sawdust and its potential use in C sequestration: Chemical and physical characterization. *Industrial Crops and Products,* **44:** 18-24, doi:10.1016/j.indcrop.2012.10.017 (2013).

2 Mašek, O. *et al.* Microwave and slow pyrolysis biochar—Comparison of physical and functional properties. *Journal of Analytical and Applied Pyrolysis,* **100:** 41-48, doi:10.1016/j.jaap.2012.11.015 (2013).

3 Yang, X. *et al.* Thermal Properties of Biochars Derived from Waste Biomass Generated by Agricultural and Forestry Sectors. *Energies,* **10:** 469, doi:10.3390/en10040469 (2017).

4 Parmar, A., Nema, P. K. & Agarwal, T. Biochar production from agro-food industry residues: a sustainable approach for soil and environmental management. *Current Science,* **107:** (2014).

5 Ghaneian, M. T. *et al.* Biosorption of hexavalent chromium from aqueous solution onto pomegranate seeds: kinetic modeling studies. *International Journal of Environmental Science and Technology,* **14:** 331-340, doi:10.1007/s13762-016-1216-8 (2017).

6 Agrafioti, E., Kalderis, D. & Diamadopoulos, E. Arsenic and chromium removal from water using biochars derived from rice husk, organic solid wastes and sewage sludge. *J Environ Manage,* **133:** 309-314, doi:10.1016/j.jenvman.2013.12.007 (2014).

7 Kołodyńska, D. *et al.* Kinetic and adsorptive characterization of biochar in metal ions removal. *Chemical Engineering Journal,* **197:** 295-305, doi:http://dx.doi.org/10.1016/j.cej.2012.05.025 (2012).

8 Kim, K. H., Kim, J. Y., Cho, T. S. & Choi, J. W. Influence of pyrolysis temperature on physicochemical properties of biochar obtained from the fast pyrolysis of pitch pine (Pinus rigida). *Bioresource technology,* **118:** 158-162, doi:10.1016/j.biortech.2012.04.094 (2012).

9 Demirbas, A. Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues. *Journal of Analytical and Applied Pyrolysis,* **72:** 243-248, doi:http://dx.doi.org/10.1016/j.jaap.2004.07.003 (2004).

10 Cao, X. & Harris, W. Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. *Bioresource technology,* **101:** 5222-5228, doi:10.1016/j.biortech.2010.02.052 (2010).

11 Woolf, D., Amonette, J. E., Street-Perrott, F. A., Lehmann, J. & Joseph, S. Sustainable biochar to mitigate global climate change. *Nature communications,* **1:** 56, doi:10.1038/ncomms1053 (2010).

12 Inyang, M. *et al.* Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass. *Bioresource technology,* **110:** 50-56, doi:10.1016/j.biortech.2012.01.072 (2012).

13 Park, D., Lim, S. R., Yun, Y. S. & Park, J. M. Reliable evidences that the removal mechanism of hexavalent chromium by natural biomaterials is adsorption-coupled reduction. *Chemosphere,* **70:** 298-305, doi:10.1016/j.chemosphere.2007.06.007 (2007).

14 Fendorf, S., Wielinga, B. W. & Hansel, C. M. Chromium Transformations in Natural Environments: The Role of Biological and Abiological Processes in Chromium(VI) Reduction. *International Geology Review,* **42:** 691-701, doi:10.1080/002068 10009465107 (2000).

15 Wang, C. *et al.* Sorption behavior of Cr(VI) on pineapple-peel-derived biochar and the influence of coexisting pyrene. *International Biodeterioration & Biodegradation,* **111:** 78-84, doi:10. 1016/j.ibiod.2016.04.029 (2016).

16 Zheng, H., Wang, Z., Zhao, J., Herbert, S. & Xing, B. Sorption of antibiotic sulfamethoxazole varies with biochars produced at different temperatures. *Environmental pollution,* **181:** 60-67, doi:10.1016/j.envpol.2013.05.056 (2013).

17 Hsu, L. C. *et al.* Cr(VI) removal on fungal biomass of Neurospora crassa: the importance of dissolved organic carbons derived from the biomass to Cr(VI) reduction. *Environmental science & technology,* **44:** 6202-6208, doi:10.1021 /es1017015 (2010).

18 Park, D., Lim, S. R., Yun, Y. S. & Park, J. M. Development of a new Cr(VI)-biosorbent from agricultural biowaste. *Bioresource technology,* **99:** 8810-8818, doi:10.1016/j.biortech.2008.04.042 (2008).

19 Karim, A., Kumar, M., Mohapatra, S., Panda, C. & Singh, A. Banana Peduncle Biochar: Characteristics and Adsorption of Hexavalent Chromium from Aqueous Solution. *International Research Journal of Pure and Applied Chemistry,* **7:** 1-10, doi:10.9734/irjpac/2015/16163 (2015).

20 Chen, T., Zhou, Z., Xu, S., Wang, H. & Lu, W. Adsorption behavior comparison of trivalent and hexavalent chromium on biochar derived from municipal sludge. *Bioresource technology,* **190:** 388-394, doi:10.1016/j.biortech.2015.04.115 (2015).

21 Yu, X. Y., Ying, G. G. & Kookana, R. S. Reduced plant uptake of pesticides with biochar additions to soil. *Chemosphere,*

76: 665-671, doi:10.1016/j.chemo sphere.2009.04.001 (2009).

22 Shrestha, G., Traina, S. J. & Swanston, C. W. Black Carbon's Properties and Role in the Environment: A Comprehensive Review. *Sustainability,* **2:** 294-320, doi:10.3390/su2010294 (2010).

23 Jiang, T. Y., Jiang, J., Xu, R. K. & Li, Z. Adsorption of Pb(II) on variable charge soils amended with rice-straw derived biochar. *Chemosphere,* **89:** 249-256, doi:10.1016/j.chemosphere.2012.04.028 (2012).

24 Stella Mary, G. *et al.* Production, characterization and evaluation of biochar from pod (Pisum sativum), leaf (Brassica oleracea) and peel (Citrus sinensis) wastes. *International Journal of Recycling of Organic Waste in Agriculture,* **5:** 43-53, doi:10.1007/s40093-016-0116-8 (2016).

25 JU; Okoli, Ibe Zuma. Adsorption Studies of Heavy Metals by Low-Cost Adsorbents. *J. Appl. Sci. Environ. Manage,* **18:** doi:10.4314/jasem.v18i3.11 (2014).

26 Claudia vargas, P. F. B. B., Elianna Castillo. Bioadsorpetion using compost : An alternative for removal of chromium (VI) from aqueous solution. *BioResources,* **7:** 2711-2727 (2012).

27 P. Miretzkya & Cirelli, A. F. Cr(VI) and Cr(III) Removal from Aqueous Solution by Raw and Modified Lignocellulosic Materials: A Review. *Journal of hazardous materials,* **180:** 1-19, doi:10.1016/j.jhazmat.2010.04.060 (2010).

28 Zhou, L. *et al.* Investigation of the adsorption-reduction mechanisms of hexavalent chromium by ramie biochars of different pyrolytic temperatures. *Bioresource technology,* **218:** 351-359 (2016).

29 Reddy, M. C., Sivaramakrishna, L. & Reddy, A. V. The use of an agricultural waste material, Jujuba seeds for the removal of anionic dye (Congo red) from aqueous medium. *Journal of hazardous materials,* **203-204:** 118-127, doi:10.1016/j.jhazmat.2011.11.083 (2012).

30 Belattmania, Z. *et al.* Protonated Biomass of the Brown Seaweed Cystoseira tamariscifolia: A Potential Biosorbent for Toxic Chromium Ions Removal. *Research Journal of Environmental Sciences* **12**, 106-113 (2018).

31 Hameed, B. H. Evaluation of papaya seeds as a novel non-conventional low-cost adsorbent for removal of methylene blue. *Journal of hazardous materials,* **162:** 939-944, doi:10.1016/j.jhazmat.2008.05.120 (2009).

32 Shrivastva, A. K. P. a. V. S. Alternanthera bettzichiana Plant powder as Low Cost adsorbent for removal of congo red from aqueous solutions. *International Journal of ChemTech Research,* **2:** (2010).

33 Albadarin, A. B. *et al.* Biosorption of toxic chromium from aqueous phase by lignin: mechanism, effect of other metal ions and salts. *Chemical Engineering Journal,* **169:** 20-30 (2011).

34 Cantrell, K. B., Hunt, P. G., Uchimiya, M., Novak, J. M. & Ro, K. S. Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. *Bioresource technology,* **107:** 419-428, doi:10.1016/j.biortech.2011.11.084 (2012).

35 Marx, S., Chiyanzu, I. & Piyo, N. Influence of reaction atmosphere and solvent on biochar yield and characteristics. *Bioresource technology,* **164:** 177-183, doi:https://doi.org/10.1016/j.biortech.2014.04.067 (2014).

36 Zhang, X., Removal of aqueous Cr(VI) by a magnetic biochar derived from Melia azedarach wood. *Bioresource technology,* **256:** 1-10, doi:https://doi.org/10.1016/j.biortech.2018.01.145 (2018).

37 Mohan, D., Rajput, S., Singh, V. K., Steele, P. H. & Pittman, C. U., Jr. Modeling and evaluation of chromium remediation from water using low cost bio-char, a green adsorbent. *Journal of hazardous materials,* **188:** 319-333, doi:10.1016/j.jhazmat.2011.01.127 (2011).

38 Gao, H. *et al.* Characterization of Cr (VI) removal from aqueous solutions by a surplus agricultural waste—rice straw. *Journal of hazardous materials,* **150:** 446-452 (2008).

39 Zhang, J. & Zheng, P. A preliminary investigation of the mechanism of hexavalent chromium removal by corn-bran residue and derived chars. *RSC Advances,* **5:** 17768-17774 (2015).