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SUPPLEMENTARY MATERIAL TO

Removal of Pb(II) from wastewater using activated carbon prepared from the seeds of *Reptonia buxifolia*

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Powder X-ray diffraction analysis

Raw material (*Reptonia buxifollia* seeds) and ACs prepared from raw material were investigated using XRD which is illustrated in Fig. S-1. AC exhibits broad diffraction peaks at 2θ of 25° which clues for presence of graphitic carbon. However, the absence of sharp diffraction peak at 2θ of 25° reveals a predominantly amorphous structure, which is an advantageous property for well-defined porous materials.[1]

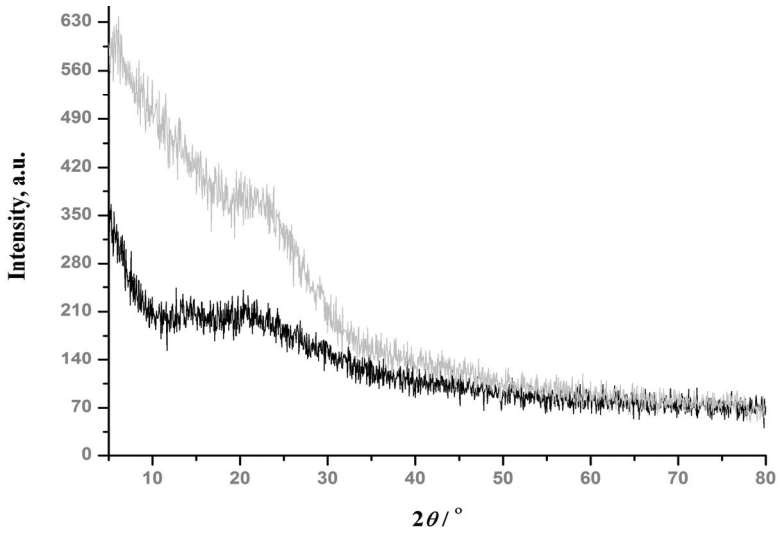

Fig. S-1. X-ray Diffraction of R. B. seeds (black) and Ac (gray).

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Fourier transform infrared (FTIR) analysis

The chemical composition of raw (R. B. seeds) and ACs prepared from raw material were determined by Fourier transform infrared (FTIR) as shown in Fig. S-2. The result of raw material shows a presence of the various functional groups which include hydroxyl groups, amines, various unsaturated hydrocarbons, aldehydes and carbonyl compounds. However, pyrolysis causes loss of some of these peaks in ACs. In raw sample the broad band was observed at 3285 cm^{-1}. This band is matched to stretching vibration of hydroxyl group on the surface. The sharp band observed at 2919 and 2850 cm^{-1} are due to the asymmetric and symmetric stretching of the methylene C–H bond respectively. However, these peaks disappeared in ACs, as ACs lost these functional groups in heat treatment. The band observed at 2162 cm^{-1} (Fig. S-3) corresponds to presence of silane (Si–H) groups.[2] The band due to silane was also retained in ACs. The band observed at 1235 cm^{-1} is matching to stretching vibration of C–O. The band found at 1627 and 1032 cm^{-1} were due to the presence of phenol. In ACs new peaks at 1404 cm^{-1} is observed which might be due to the carbonate group develop in ACs.

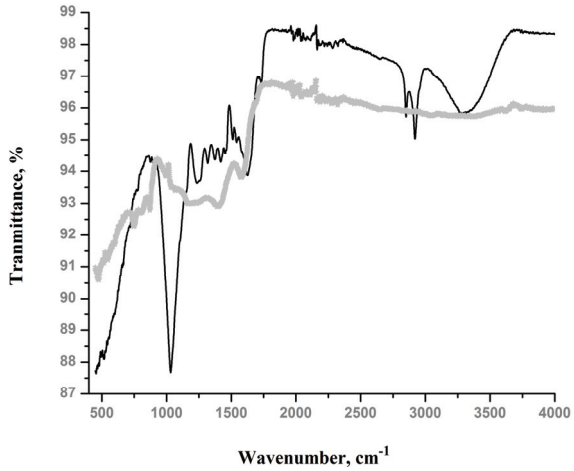

Fig. S-2. FTIR spectra of R. B. seeds (black) material and AC (gray).

Pseudo-1st order kinetic equation

A pseudo-1st-order kinetic model successfully explains the kinetics of many adsorption systems. The Lagergren equation is given as follows.[3]

$$\ln (Q_e - Q_t) = \ln Q_e - K_1 t \quad (1)$$

where Q_t is the amount of Pb^{+2} adsorbed (mg/g) at any time t, Q_e is the amount of Pb^{2+} adsorbed (mg/g) at equilibrium, and K_1 is the rate constant.

The value of K_1 can be evaluated from the intercept and slope of the linear plot of $\ln (Q_e - Q_t)$ against time t as shown in Fig. S-3. The value of correlation

coefficient R^2 was found to be 0.687 and 0.824 for biomass and activated carbon, respectively. The value of R^2 obtained suggests that the adsorption of Pb^{2+} on biomass does not follow the pseudo-first-order kinetics.

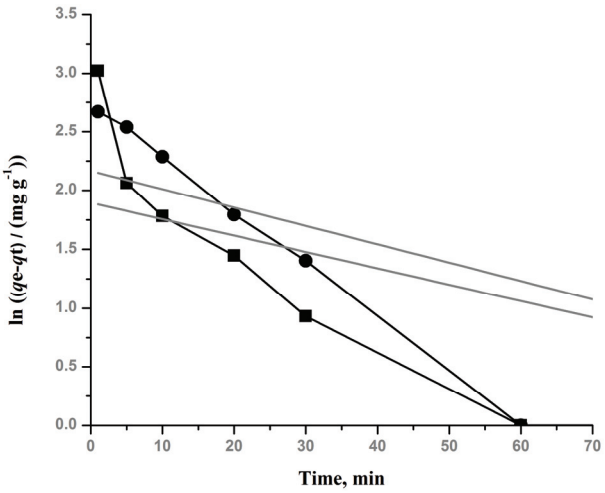

Fig. S-3. Pseudo-first-order kinetic plot for the biosorption of Pb^{+2} on raw R. B. seeds (■) and AC (●).

Adsorption models

TABLE S–I. Comparison of adsorption parameters calculated using Langmuir isotherm for adsorption of Pb(II) on adsorbents

Constant	Adsorbent	
	R. B. seeds	AC
R^2	0.99	0.998
K_L / dm^3 mg^{-1}	0.01	0.10
R_L	0.23	0.02
Q_m / mg g^{-1}	259.97	525.78

TABLE S-II. Comparison of adsorption parameters calculated using Freundlich isotherm for adsorption of Pb(II) on adsorbents

Constant	Adsorbent	
	R. B. seeds	AC
R^2	0.95	0.87
K_F / mg g^{-1}	3.11	148.70
$1/N$	0.69	0.22

Thermodynamics of Pb^{2+} adsorption

Temperature greatly influence the adsorption phenomena. In the current study, the temperature was varied in the range of 283 to 343 K, as shown in Fig. S-4. The results revealed that adsorption decreases as the temperature were increased. From these results, it is concluded that adsorption of Pb(II) on AC is physiosorption in nature. The negative value of enthalpy change (Table S-III) suggests that Pb(II) adsorption, on AC is an exothermic process. The adsorption decreased with an increase in temperature. The spontaneity of the Pb(II) adsorption on the R.B seeds and AC were estimated by varying thermodynamic parameters, such as, the free energy change (ΔG) and K by the following equation:[4, 5]

$$\Delta G = -RT \ln K \tag{2}$$

where K is the equilibrium constant and determined as:

$$K = \frac{A_s}{A_e} = \frac{V_s C_s}{V_e C_e} \tag{3}$$

where C_s represents Pb(II) amount adsorbed per mass of adsorbent (mol/g) and C_e shows the Pb(II) concentration in solution at equilibrium (mol/ml), A_s is the activity of adsorbed Pb(II), A_e is the activity of the Pb(II) in solution at equilibrium, V_s is the activity coefficient of the adsorbed Pb(II) and V_e is the activity coefficient of the Pb(II) in solution. The K values were used to determine ΔG, ΔH and ΔS.

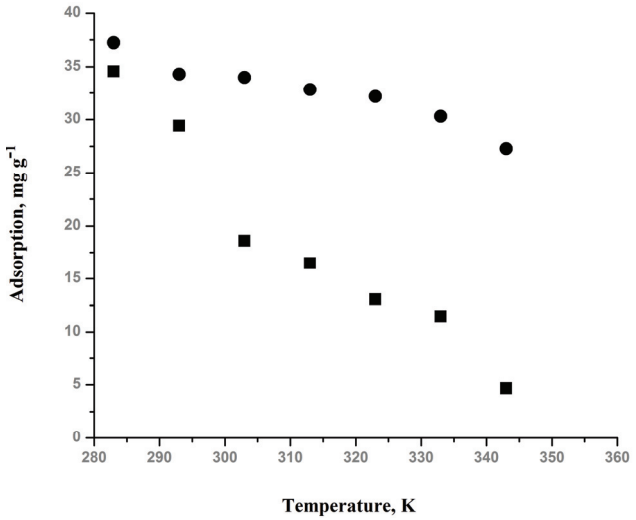

Fig. S-4. Effect of temperature of Pb(II) biosorption on R. B. seeds (■) and AC (●).

The average enthalpy change (ΔH) of the system was calculated by using Van't Hoff equation:

$$(\ln K)\,T_2 - (\ln K)\,T_1 = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (4)$$

where T_2 represents the final temperature and T_1 represents initial temperature. The entropy change (ΔS) can be obtained by the equation:

$$\Delta S = \frac{\Delta G - \Delta H}{T} \quad (5)$$

The thermodynamic parameters of R. B. seeds and AC are listed below in Tables S-III and S-IV, respectively. A negative standard free energy change shows that the adsorption reaction is a spontaneous and reversible process. Greater negative value of free energy change for AC further support the higher adsorption of Pb(II) on AC. The value of free energy change, for AC, prepared from R. B. seeds give similar results revealed in the adsorption of Pb(II) on *Mucor rouxii* biomass.[6] While, the adsorption of Pb(II) on raw R. B. seeds is matching with HNO_3-modified *P. americana* bioadsorbent.[7]

TABLE S-III. Thermodynamic parameters values for Pb(II) adsorption on raw R.B seeds

Thermodynamic constant	Temperature, K						
	283	293	303	313	323	333	343
K / mL g^{-1}	1118.12	713.59	295.93	245.60	176.77	149.01	51.51
ΔG / kcal mol^{-1}	–3.95	–3.83	–3.43	–3.42	–3.32	–3.31	–2.69
ΔH / kcal mol^{-1}	–8.87	–8.87	–8.87	–8.87	–8.87	–8.87	–8.87
ΔS / kcal mol^{-1} K^{-1}	–0.02	–0.02	–0.02	–0.02	–0.02	–0.02	–0.02

Table S-IV**.** Various thermodynamic parameters values for Pb(II) adsorption on AC

Thermodynamic constant	Temperature, K						
	283	293	303	313	323	333	343
K / m L g^{-1}	1459.2	1091.34	1061.72	955.69	902.60	769.29	600.35
ΔG / kcal mol^{-1}	–4.097	–4.07	–4.195	–4.27	–4.37	–4.397	–4.36
ΔH / kcal mol^{-1}	–2.42	–2.42	–2.42	–2.42	–2.42	–2.42	–2.42
ΔS / kcal mol^{-1} K^{-1}	0.006	0.006	0.006	0.006	0.006	0.006	0.006

REFERENCES

1. M. S. Shamsuddin, N. R. N. Yusoff, M. A. Sulaiman, *Procedia Chem.* **19** (2016) 558 (https://doi.org/10.1016/j.proche.2016.03.053)
2. D. B. Kapgate, C. Das, D. Basu, A. Das, G. Heinrich, *J. Elastomers Plast.* **47** (2013) 248 (http://jep.sagepub.com/content/early/2013/10/22/0095244313507807)
3. Z. A. Jamiu, T. A. Saleh, S. A. Ali, *RSC Adv.* **5** (2015) 42222 (https://doi.org/10.1039/C5RA05447H)
4. Ç. Arpa, E. Başyilmaz, S. Bektaş, Ö. Genç, Y. Yürüm, *Fuel Process. Technol.* **68** (2000) 111 (https://doi.org/10.1016/S0378-3820(00)00126-0)
5. A. E. Ofomaja. *Bioresour. Technol.* **101** (2010) 5868 (https://doi.org/10.1016/j.biortech.2010.03.033)

6. S. S. Majumdar, S. K. Das, R. Chakravarty, T. Saha, T. S. Bandyopadhyay, K. Guha, *Desalination* **251** (2010) 96 (https://doi.org/10.1016/j.desal.2009.09.137)
7. G. Wangab, S. Zhanga, P. Yaoa, Y. Chena, X. Xua, T. Lia, G. Gong, *Arab. J. Chem.* **11** (2018) 99 (https://doi.org/10.1016/j.arabjc.2015.06.011).