Modification and Application of *Albizia lebbeck* Sawdust For The Sorption of Lead(II) and Copper(II) From Aqueous Solutions

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ABSTRACT

Sawdust of *Albizia lebbeck* (locally known as koroi) was modified by treatment with sodium methylate followed by reactions with epichlorohydrin and n-dodecylamine to afford the sorbent which was termed as DDA-SD. The sorbent was characterized with the help of FTIR (ATR), SEM and chemical test. It was then used for the sorption of Pb\(^{2+}\) and Cu\(^{2+}\) from aqueous solutions and the effects of solution pH, dosage of sorbent, initial metal ions concentration and contact time were enumerated. The sorption data were tested for Langmuir and Freundlich isotherm models and found that the process followed Langmuir model and the maximum sorption capacities were calculated as 17.37 mg/g and 9.4 mg/g for Pb\(^{2+}\) and Cu\(^{2+}\) ions respectively. The sorption data were also tested for pseudo-first order and pseudo-second order kinetic models and the data fitted well with pseudo second order kinetics. Exhausted DDA-SD adsorbent can be regenerated using 0.1M HCl or 0.1M HNO\(_3\) followed by wash with deionized water and reused for further adsorption purpose.

**Keywords:** Non-biodegradable, Etherification, Epichlorohydrin, Epoxy moiety, Morphology.

INTRODUCTION

Disposal of untreated industrial wastes is the major source of heavy metals contamination, which causes severe water, soil and air pollution. The persistent nature of heavy metals results their accumulation in plants and animal tissues and ultimately enter the food chain. When heavy metals enter into human body through contaminated foods, they are bio-amplified and cause serious threat to
the public health. From various industrial activities lead and copper are exposed to the environment and cause detrimental effects such as malfunction of brain, cognitive disorder to the children, renal diseases, anemia and loss of reproductive power. Many techniques such as precipitation, ion-exchange, membrane separation, electrodialysis, extraction etc. are reported for removing heavy metals. However, these techniques are not attractive because of high cost and difficulties associated with the handling of toxic sludges produced during the processes. Adsorption processes have drawn much attention due to their high efficacy in removing heavy metals and availability of a wide variety of adsorbents such as activated carbon, and metal oxides as activated carbon. An adsorbent prepared by oxidation of pure cellulose with periodate and hydroxamic acid demonstrated excellent Cu adsorption capacity of 246 mg/g.

To the best of our knowledge no report is available on the development of adsorbent for heavy metal by modification of sawdust using etherification followed by ring opening by an alkyl amine strategy. In the present investigation modification of sawdust of *Albizia lebbeck* was carried out by treatment with sodium methylate, followed by etherification using epichlorohydrin and oxirane ring opening by n-dodecylamine to afford a material, which was applied for the sorption of Cu and Pb ions.

**MATERIALS AND METHODS**

**Materials and reagents**

Sawdust of *Albizia lebbeck* (Local name Koroi) obtained from a sawmill located at Mirpur in Dhaka, Bangladesh was washed with water and sun-dried for 3 days followed by drying in an oven at 50°C for 72 h and cooled in desiccators. The dried material was sieved and the fraction with a particle size between 0.2 and 0.6 mm was used for the preparation of chemically modified adsorbent. Chemical analyses of dried sawdust were carried out using literature methods and found that it contained 7.25% extractible materials, 68.7% cellulose and 17% lignin.

Sodium methylate, dimethylsulfoxide (DMSO), epichlorohydrin, ethanol, n-dodecylamine, copper sulfate pentahydrate, lead nitrate, sodium hydroxide and nitric acid were purchased from Aldrich and used as received. Stock solutions of the metals were obtained by dissolving required amounts of CuSO₄·5H₂O and Pb(NO₃)₂ in deionized (DI) water. A small volume (10-20 μL) of 0.1M NaOH or 0.1M HNO₃ were added to the metal ions solutions to adjust the pH.

**Preparation of the adsorbent**

Modification of sawdust was carried out following a literature procedure. In brief, sawdust (5.0 g) was suspended in DMSO (100 mL), purged with N₂ and stirred in a hot plate magnetic stirrer.
for 2 h at 60°C. The mixture was cooled to room temperature, treated with sodium methylate (15.0 g) and stirred for 1 h in N₂ atmosphere. The resulting solids were separated by filtration and washed with DI water (200 mL) and dried at 50°C for 3 h to afford the material NaO-SD (4.5 g). To the suspension of NaO-SD (3.0 g) in DMSO (50 ml) epichlorohydrin (30 mL) was added and stirred for 2 h at 50°C in N₂ atmosphere. Solid materials thus obtained were separated by filtration and washed with DI water (200 mL) and dried at 50°C for 3 h to afford the material NaO-SD (4.5 g). To the suspension of NaO-SD (3.0 g) in DMSO (50 ml) epichlorohydrin (30 mL) was added and stirred for 2 h at 50°C in N₂ atmosphere. Solid materials thus obtained were separated by filtration and washed with DI water and dried at 50°C for 3 h to afford ECH-SD (3.12 g). ECH-SD (1.4 g) was suspended in DMSO (30 mL), n-dodecylamine (3.2 g) was added in portions and heated at 100°C with stirring for 18 hours. The final material was separated by filtration and washed with DI water in an oven at 50°C for 3 h and cooled in desiccators to afford the sorbent DDA-SD (1.4 g).

Instruments
The functional groups present in the sorbent (DDA-SD) were identified by FTIR-ATR (Shimadzu, Japan) and the surface morphology of it was determined using a scanning electron microscope (Philips XL30, FEI, USA). The surface area was determined by BET analysis, which was performed on a Quantachrome Autosorb-1. For BET experiment DDA-SD sample were out gassed at 120°C for 24 h before analysis and Krypton gas was used as the adsorbent. To obtain a value of surface area, 11 points were measured in the standard range of (P/Po) = 0.05 to 0.3. The pH of the solutions was measured with a pH meter (HI 2211-02, Hanna, Romania). Batch adsorption experiments were performed under shaking in an orbital Shaker (SSL1, Stuart UK). Metal ions concentrations of the filtered solutions (Whatman 41) were measured with Atomic Absorption Spectroscopy (AAS) (Varian AA 240 FS, USA).

Batch sorption experiments
Metal uptake capacities of the DDA-SD were investigated by adding different amounts of the DDA-SD (50-350 mg) to 100 mL metal ion solutions of fixed concentration (25.0 ppm) in different conical flasks, pH were adjusted 5.8 and 7.1 for Pb²⁺ and Cu²⁺ respectively. Effect of contact time was monitored by adding fixed amount of the sorbent (500 mg) to metal ion solutions of concentrations of 23.5, 38.0 ppm for Cu²⁺ and 9.5, 28.5 ppm for Pb²⁺ and pH were maintained at 5.8 for Pb²⁺ and 7.1 for Cu²⁺ and left under shaking. Aliquots of 2 mL were drawn at different time intervals and metal ion concentrations were measured by AAS.

Desorption study
Desorption study was conducted by soaking 20 mg of the exhausted DDA-SD in 20 mL of 0.1M HNO₃ or 0.1M HCl and left under shaking for 3 hours. An aliquot of 0.5 mL was drawn in every 30 min and metal ion concentrations were analyzed using AAS.

RESULTS AND DISCUSSION
Synthesis of the adsorbent
The major chemical constituents of sawdust are cellulose, lignin and hemicellulose. The reactions occurred during the modification process are represented in the scheme 1. The primary hydroxyl group of the β unit (1-4 linked D-glucose) of cellulose reacted with sodium methylate to afford Cell-CH₂-ONa (NaO-SD). During treatment with sodium methylate in DMSO a considerable amount of extractible materials, hemicellulose and lignin were removed from the cellulosic material. Cell-CH₂-ONa then reacted with epichlorohydrin to afford cellulose derivative containing oxirane moiety (ECH-SD). The

Where Ci and Ce stand for initial and equilibrium concentrations of the metal ion (g/L), m represents mass of the adsorbent (g) and V is the volume of the solution (L).

Effect of dosage was investigated by adding different amounts of the DDA-SD (50-350 mg) to 100 mL metal ion solutions of fixed concentration (25.0 ppm) in different conical flasks, pH were adjusted 1.9-6 for Pb(II) and 3-10.2 for Cu(II) by adding dilute nitric acid or sodium hydroxide and 100 mg of DDA-SD was added to each flask and left under shaking for 1 hour. Afterwards sorbents were separated by filtration and sorption capacities were calculated using the equation (1).

Desorption study
Desorption study was conducted by soaking 20 mg of the exhausted DDA-SD in 20 mL of 0.1M HNO₃ or 0.1M HCl and left under shaking for 3 hours. An aliquot of 0.5 mL was drawn in every 30 min and metal ion concentrations were analyzed using AAS.
oxirane ring was opened by reaction with n-dodecyl amine to afford the sorbent (DDA-SD).

Scheme 1. Modification of sawdust

Characterization

FTIR Analysis: FTIR analysis of NaO-SD, ECH-SD and DDA-SD were carried out using ATR sampling technique and vibrational frequencies are summarized in the Table 1.

Table 1: FTIR peaks for synthesized materials

| Material   | ν cm⁻¹                  |
|------------|-------------------------|
| NaO-SD     | 3587-3033, 2925-2825, 1590, 1508, 1458, 1420, 1325, 1262, 1218, 1016, 638. |
| ECH-SD     | 3700-3400, 2976, 2888, 1458, 1388, 1250, 1155, 1073, 954, 821, 638.           |
| DDA-SD     | 3700-3490, 2976, 2888, 1458, 1388, 1250, 1155, 1073, 954, 821, 669, 638.       |

For NaO-SD the prominent peaks appeared at 1016 (strong), 1250, 1458, 2825-2925 and 3033-3587 cm⁻¹ which are assignable to the C-O, C-C, C-H, and OH stretching vibrations of the cellulose moiety. For ECH-SD the C-O, C-C, C-H, and OH stretching vibrations were observed at 1073, 1250, 1458, 2888, 2976 and 3400-3700 cm⁻¹, while those peaks for DDA-SD were at 1073, 1250, 1458, 2888, 2976 and 3490-3700 cm⁻¹. New peaks at 954 and 821 cm⁻¹ were present in case of ECH-SD and DDA-SD which are assignable to the presence of the oxirane moiety.

The presence of an epoxy group in the ECH-SD was further confirmed by a chemical method. On the treatment of ECH-SD with sodium thiosulfate the oxirane ring breaks down and liberates an equimolar amount of NaOH which can be quantified by titration with standardized HCl in presence of phenolphthalein indicator. Using this strategy the amount of epoxide ring (mg) per gm of DDA-SD was determined by using the following equation (2). The amount of epoxide moiety was found to be 0.37 mg/g which was in good agreement with the previous result.

\[
\text{Epoxide} = \frac{V \times M \times 58 \times 1000}{W}
\]

Where V = Volume (mL) of HCl required, M = molarity of HCl, W = Weight (gm) of treated sawdust (ECH-SD).

SEM Analysis

SEM images of NaO-SD and DDA-SD revealed similar morphology with rough surfaces in both cases (Figure 2).
Surface Area

The surface area of NaO-SD and DDA-SD were measured by BET analysis and found to be 0.75 m$^2$/g and 0.73 m$^2$/g respectively, which revealed that the materials have comparable surface areas.

Effect of pH

Depending on the pH of the solution the surface charge of an adsorbent varies significantly, which plays a vital role in the sorption process. The effect of pH on the sorption of Pb$^{2+}$ and Cu$^{2+}$ was studied by adding a constant dosage of DDA-SD (20 mg/20 mL) into and metal ion solutions of fixed concentrations (50 ppm for Pb$^{2+}$ and 5 ppm for Cu$^{2+}$) in different conical flasks maintaining pH in the range of 1.9 to 10. The result showed that with increasing pH the sorption of Pb$^{2+}$ increased dramatically and reached the maximum at pH 5.9. Effect of further increase of pH was not monitored as Pb$^{2+}$ precipitated beyond the pH of 5.9. In case of Cu$^{2+}$ the maximum sorption was achieved at pH 7.1 and it remained same up to the pH 10. It is assumed that at low pH some of the NH groups of DDA-SD were protonated, which hindered the chelation of metal ions and resulted lower sorption (Scheme 3).

Effect of Time

The equilibration time is considered as the optimum contact time, which was determined by measuring the sorption capacities at different time.

Effect of dosages

The effect of dosages on the sorption of Pb$^{2+}$ was carried out using DDA-SD dosages ranging from 0.5 g/L to 3.5 g/L at pH 5.85 and at room temperature. The experiments were carried out under shaking in an orbital shaker at rpm 180 for 1 hours. The change in removal efficiency (%R.E) and sorption capacity of DDA-SD for Pb$^{2+}$ with the adsorbent dosages are shown in the Figure 4.
Adsortion isotherms

The relationship between the amount of sorbate attached on the surface of a sorbent and its concentration in the equilibrium solution at a constant temperature is represented by sorption isotherm. Fig. 6 shows the equilibrium sorption data for \( \text{Pb}^{2+} \) and \( \text{Cu}^{2+} \) on DDA-SD.

The relationship between the equilibrium sorption capacities, \( q_e \) (mg/g) with the metal ion concentrations at equilibrium, \( C_e \) (mg/L) can be obtained by using Langmuir (equ. 3) and Freundlich (equ. 4) isotherm models.

\[
\frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + \frac{1}{q_{\text{max}}K_L}
\]

Where \( C_e \) is the equilibrium concentration of sorbate (mg. L\(^{-1}\)); \( q_e \) is the equilibrium sorption capacity (mg. g\(^{-1}\)); \( q_{\text{max}} \) is the maximum monolayer sorption capacity (mg. g\(^{-1}\)) and \( K_L \) is Langmuir constant (L. mg\(^{-1}\)).

From the slope and intercept of the Langmuir plot the values of \( K_L \) and \( q_{\text{max}} \) were calculated and shown in the Fig. 7 and Table 2. The maximum sorption capacities were 17.37 mg/g and 9.4 mg/g for \( \text{Pb}^{2+} \) and \( \text{Cu}^{2+} \) respectively. It was clear that sorption process of both \( \text{Pb}^{2+} \) and \( \text{Cu}^{2+} \) on DDA-SD followed Langmuir isotherm which was attributed to the fact that the sorption occurred through the formation of monolayer at homogeneous surface of the sorbent and there was no transmigration of sorbate particles during the process.

A dimensionless parameter known as separation factor (\( R_L \)) was obtained from the Langmuir constant, \( K_L \) using the equation (4).

\[
R_L = \frac{1}{1 + K_L C_i}
\]

Where \( C_i \) is the initial concentration of the metal ion (mg/L) and \( K_L \) is the Langmuir constant (L/mg).
R_L values indicate the feasibility of the sorption process, thus R_L = 0, 0 < R_L < 1, R_L = 1 and R_L > 1 indicate that the process is irreversible, favourable, linear and unfavourable respectively. The values of R_L in the present study were between 0 and 1 (Table 3) and indicated that the sorption process was favourable.

The sorption data were then evaluated for Freundlich model using the equation (5).

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  
(5)

The Freundlich constant, K_F indicates sorption capacity, while 1/n is a function of the energy of sorption process. It is evident from the Fig. 8 that the sorption process did not follow Freundlich isotherm model indicating that the processes did not proceed through the formation of a multilayer on heterogeneous surface^6.

Fig. 8. Freundlich isotherms for sorption of Pb^{2+} and Cu^{2+} on DDA-SD

**Sorption Kinetics**

To understand the kinetics of the sorption of Pb^{2+} and Cu^{2+} on DDA-SD, the pseudo first order (equ. 6) and pseudo second order (equ. 7) kinetic equations were tested for the sorption data.

\[ \log (q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \]  
(6)

According to the equation 6, \( \log (q_e - q_t) \) versus t was plotted and observed that the sorption data for neither Pb^{2+} nor Cu^{2+} (not shown) matched with the first order kinetics (Figure 9).

\[ \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \]  
(7)

The second order kinetics model was tested by plotting t/q_t versus t and it was evident that the sorption of both Pb^{2+} and Cu^{2+} on DDA-SD perfectly followed this kinetic model \( (R^2 = 0.9966 \text{ to } 0.9998) \). This means that the sorption rate depends on the metal ion concentration as well as the number of available active sites of the sorbent. The sorption capacities of DDA-SD were calculated from the pseudo-second-order kinetics plots and listed in the Table 4 and found that the sorption capacities were similar to those obtained from Langmuir isotherm model.

**Table 4: Adsorption capacities of DDA-SD**

| Metal  | Initial conc. (ppm) | R^2 | Ads. capacity, q_e (mg/g) |
|--------|---------------------|-----|--------------------------|
| Pb^{2+}| 28.5                | 0.9966 | 18                      |
|        | 18                  | 0.9875 | 14                      |
|        | 9.5                 | 0.9963 | 8                       |
| Cu^{2+}| 38                  | 0.9994 | 17.7                    |
|        | 23.4                | 0.9998 | 11.1                    |
Regeneration

In this study, regeneration of the sorbent was carried out by soaking 20 mg of exhausted DDA-SD in 20 mL 0.1M HNO₃ or 0.1M HCl and leaving it for 30 min followed by wash with DI water. The desorption ratio (DR) was calculated as follows.

\[
DR = \frac{\text{amount of metal ion (mg) desorbed/ mg DDA-SD}}{\text{amount of metal ion (mg) adsorbed/ mg DDA-SD}}
\]

After 30 min the desorption ratio was 0.97 for both the acid solutions used for regeneration purpose. Further increase in time decreased the desorption ratio, which may be due to the re-adsorption of the metal ions on regenerated DDA-SD.

The regenerated DDA-SD was reused for sorption of \(\text{Pb}^{2+}\) and it was found that in case of 34.0 ppm solution the removal efficiency of regenerated DDA-SD was 30.4%, 29% and 27% for 1st, 2nd and 3rd recycle while removal efficiency of fresh DDA-SD was 49.5%. The decrease of removal efficiency of the regenerated DDA-SD is attributed to the reduction of active site due to protonation of the NH functional group in the acidic solution, which is assumed to be responsible for metal ion sorption.

In the present investigation sawdust of \(\text{Albizia lebbeck}\) was modified chemically and the sorption characteristics of the material were studied under equilibrium conditions using \(\text{Pb}^{2+}\) and \(\text{Cu}^{2+}\) solutions. The optimum pH for the sorption of \(\text{Pb}^{2+}\) and \(\text{Cu}^{2+}\) were 5.9 and 7.1 respectively. The sorption data fitted well to Langmuir model and did not fit Freundlich model at all. The maximum sorption capacities of \(\text{Pb}^{2+}\) and \(\text{Cu}^{2+}\) on DDA-SD were 17.37 and 9.4 mg/g respectively. The sorption data fitted well with the second order kinetic model. The exhausted DDA-SD was regenerated by treating with either 0.1M HNO₃ or 0.1M HCl followed by washing with DI water and the regenerated DDA-SD showed acceptable sorption capacities.

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**Conflict of Interest**

The authors declare that there is no conflict of interest.

**REFERENCES**

1. Ahalya N.; Ramachandra TV.; Kanamadi RD., Biosorption of heavy metals. *Res. J. Chem. Environ.*, 2003, 7(4), 71-78.
2. Nouri J.; Lorestani B.; Yousefi N.; Khorsan N.; Hasani AH.; Seif S.; Cheraghi M., Phytoremediation potential of native plants grown in the vicinity of Ahangaran lead–zinc mine (Hamedan, Iran). *Environ. Earth Sci.*, 2011, 62(3), 639-644.
3. Pagliuca A.; Mufi GJ., Lead Poisoning: an age-old problem. *British Med. J.*, 1990, 300, 830.
4. O’Connell DW.; Birkinshaw C.; O’Dwyer TF.; Heavy metal adsorbents prepared from the modification of cellulose: A review. *Bioresour Technol.*, 2008, 99, 6709–6724.
5. Namaisvayam C.; Ranganathan K. Removal of \(\text{Pb}^{2+}\), \(\text{Cd}^{2+}\) and \(\text{Ni}^{2+}\) and mixture of metal ions by adsorption onto waste \(\text{Fe}^{3+}/\text{Cr}^{3+}\) hydroxide and fixed bed studies. *Envirol. Technol.*, 1995, 16, 851–860.
6. Gueu S.; Yao B.; Adouby K.; Ado GW., Kinetics and thermodynamics study of lead adsorption on to activated carbons from coconut and seed hull of the palm tree. *Int. J. Environ. Sci. Technol.*, 2007, 4(1), 11-17.
7. Nouri S.; Haghseresht F.; Lu GQM., Comparison of adsorption capacity of p-cresol & p-nitrophenol by activated carbon in single and double solute. Adsorption., 2002, 8, 215–223.

8. Celis R.; Carmen HM.; Cornejo J., Heavy metal adsorption by functionalized clays. Environ. Sci. Technol., 2000, 34, 4593–4599.

9. Abollino O.; Malandrino M.; Sarzanini C.; Mentasti E., Adsorption of heavy metals on Na- montmorillonite effect of pH and organic substances. Water Res., 2003, 37, 1619–1627.

10. Oliveira LCA.; Petkowicz DI.; Smaniotto A.; Pergher SBC., Magnetic zeolites: a new adsorbent for removal of metallic contaminants from water. Water Res., 2004, 38, 3699–3704.

11. Zhang GS.; Qu J.H.; Liu HJ.; Liu RP.; Wu RC., Preparation and evaluation of a novel Fe-Mn binary oxide adsorbent for effective arsenite removal. Water Res., 2007, 41, 1921–1928.

12. Zhang GS.; Qu JH.; Liu HJ.; Liu RP.; Li GT., Removal mechanism of As(III) by a novel Fe-Mn binary oxide adsorbent: oxidation and sorption. Environ. Sci. Technol., 2007, 41, 4613–4619.

13. Robinson T.; Chandran B.; Nigam P., Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. Water Res., 2002, 36, 2824–2830.

14. Saeed A.; Akhter MW.; Iqbal M., Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. Sep. Purif. Technol., 2005, 45, 25–31.

15. Babarinde NAA.; Babalola JO.; Sanni RA., Biosorption of lead ions from aqueous solution by maize leaf. Intl. J. Phys. Sci., 2006, 1, 23–26.

16. King P.; Srivinas P.; Kumar YP.; Prasad VSRK., Sorption of copper(II) ion from aqueous solution by Tectona grandis l.f. (teak leaves powder). J. Hazard. Mater., 2006, 136, 560–566.

17. Hanafiah MAKM.; Ngah WSW.; Ibrahim SC.; Zakaria H.; Ilias WAHW., Kinetics and thermodynamic study of lead adsorption onto rubber (Hevea brasiliensis) leaf powder. J. Appl. Sci., 2006, 6, 2762–2767.

18. Hanafiah MAKM.; Ibrahim SC.; Yahya MZA., Equilibrium adsorption study of lead ions onto sodium hydroxide modified Lalang (Imperata cylindrica) leaf powder. J. Appl. Sci. Res., 2006, 2, 1169–1174.

19. Johnson PD.; Watson MA.; Brown J.; Jefcoat IA., Peanut hull pellets as a single use sorbent for the capture of Cu(II) from wastewater. Waste Manage., 2002, 22, 471–480.

20. Bhattacharya AK.; Mandal SN.; Das SK., Adsorption of Zn(II) from aqueous solution by using different adsorbents. Chem. Eng. J., 2006, 123, 43–51.

21. Loukidou MX.; Matis KA.; Zouboulis Al.; Kyriakidou ML., Removal of As(V) from wastewaters by chemically modified fungal biomass. Water Res., 2003, 37, 4544–4552.

22. Atia AA.; Donia AM.; Abou-El-Enein SA.; Yousif AM., Studies on uptake behavior of copper(II) and lead(II) by amine chelating resins with different textural properties. Sep. Purif. Technol., 2003, 33, 295–301.

23. Gaballah I.; Goy D.; Alain E.; Kibertus G.; Thauront J., Recovery of copper through decontamination of synthetic solutions using modified barks. Met. Metall. Trans. B., 1997, 28, 13–23.

24. Nakajima A.; Sakaguchi T., Recovery and removal of uranium by using plant wastes. Biomass., 1990, 21, 55–63.

25. Sciban M.; Klasnja M.; Skrbic B., Modified softwood sawdust as adsorbent of heavy metal ions from water. J. Hazard. Mater., 2006, 136, 266–271.

26. Argun ME.; Dursun S.; Ozdemir C.; Karatas M., Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. J. Hazard. Mater., 2007, 141, 77–85.

27. Acar FN.; Eren Z., Removal of Cu(II) ions by activated poplar sawdust (Samsun Clone) from aqueous solutions. J. Hazard. Mater., 2006, 137, 909–914.

28. Ashwini A.; Udayasimha L.; Vyshnavi DR.; Usha HS., Comparative study on removal of copper from aqueous solution by modified and non modified sawdust adsorption. Intl. J. Pure Appl. Math., 2018, 120(6), 6709-6725.

29. Baral SS.; Das SN.; Rath P., Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust. Biochem. Eng. J., 2006, 31, 216-222.

30. Taty-Costodes VC.; Fauduet H.; Porte C.; Delacroix A., Removal of Cd(II) and Pb(II) ions from aqueous solutions by adsorption onto sawdust of Pinus sylvestris. J. Hazard. Mater., 2003, 105, 121–142.
31. Bulut Y.; Tez Z., Removal of heavy metal ions by modified sawdust of walnut. Fresen. Environ Bull., 2003, 12, 1499-1504.
32. Choudhury TR.; Bhowmik S.; Rahman MS.; Nath MR.; Jahan FN.; Begum B.A.; Nurnabi M., Synthesis of Nano Zerovalent Iron Supported Sawdust (NZVI/SD) and Its Application for Removal of Arsenic (III) from Aqueous Solution. Chem. Sci. Int. J., 2020, 29(1), 1-12.
33. Haq AU.; Jan MR.; Shah J.; Sadia M.; Saeed M., A comparative sorption study of Ni (II) from aqueous solution using silica gel, amberlite IR-120 and sawdust. Zeitschrift für Physikalische Chemie, 2019, 233(9), 1275-1292.
34. El-Saied FA.; Abo-Elenan SA.; El-shinawy FH., Removal of lead and copper ions from polluted aqueous solutions using nano-sawdust particles. Intl J. Waste Resour., 2017, 7, 305.
35. Ogbu IC.; Akpomie KG.; Osunkunle AA., Sawdust-kaolinite composite as efficient sorbent for heavy metal ions. Bangladesh J. Sci. Ind. Res., 2019, 54(1), 99-110.
36. Navarro RR.; Sumi K.; Fujii N., Matsumura M., Mercury removal from wastewater using porous cellulose carrier modified with polyethyleneimine. Water Res., 1996, 30(10), 2488-2494.
37. Maekawa E.; Koshijima T., Preparation and characterisation of hydroxamic acid derivatives and its metal complexes derived from cellulose. J. Appl. Polym. Sci., 1990, 40, 1601–1613.
38. Yu W.; Bao-yu G.; Wen-wen Y.; Qin-yan Y., Preparation and utilization of wheat straw anionic sorbent for the removal of nitrate from aqueous solution. J. Environ. Sci., 2007, 19, 1305-1310.
39. Kamari A.; Ngah WSW., Adsorption of Cu(II) and Cr(VI) onto treated Shorea dasyphylla bark: Isotherm, kinetics and thermodynamic studies. Sep. Sci. Tech., 2010, 45(4), 486-496.
40. Hanafiah MAKM.; Ngah WSW.; Zolkafly SH.; Teong LC.; Majid ZAA., Acid Blue 25 adsorption on base treated Shorea dasyphylla sawdust: Kinetic, isotherm, thermodynamic and spectroscopic analysis. J. Environ. Sci., 2012, 24(2), 261-268.