Preparation and Characterization of Activated Carbon from *Brassica Juncea* and its Application for the Removal of Pb(II) from Ground Water at Pydibhimavaram Industrial Area, Srikakulam District, A.P.

J.V.S.K.V. Kalyani[1]*and Ch. Sudhakar[2]

1. Department of Chemistry, Vignan Institute of Information Technology, Visakhapatnam, **INDIA**
2. Department t of Chemistry, GIT, GITAM (Deemed to be University), Visakhapatnam, **INDIA**
Email: jvskvk77@gmail.com

_____

ABSTRACT

Active surface properties and high adsorption capacities containing activated carbon were prepared from Brassica juncea (ACBJ) by chemical process such as chemical activation with conc. sulphuric acid in a wt.ratio 2:1 (Biomaterial:acid).The Fourier transformation infrared spectroscopy and Scanning electron microscopy techniques were used to investigate the surface functional group and the morphology of the resulting sample. The physico chemical characteristics such as moisture, ash, conductivity, total carbon, apparent density, pH, phenol number, methylene blue, iron etc were studied for carbon content. Based on the results of the characterization studies, the activated carbon prepared by the impregnation of with sulphuric acid (30% solution followed by activation at 800 degrees centigrade) was selected as best quality adsorbent due to the highest surface area with large number of pores and low ash content for the removal of metals from aqueous solutions. The experimental results indicated that the prepared activated carbon is suitable for the removal of toxic Pb(II) from the ground waters of industrial area.

Graphical Abstract
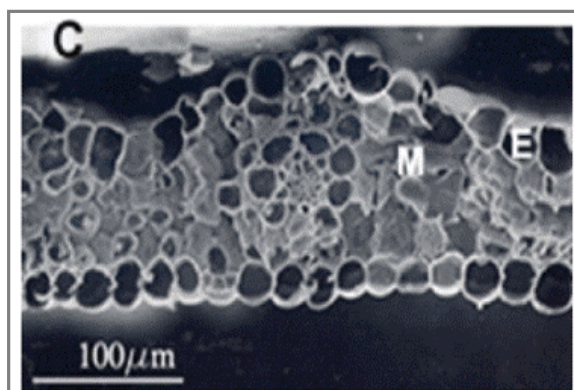
SEM Image of ACBJ (Magnification X2000)

Keywords: Activated carbon from *Brassica juncea*, FTIR, SEM, Adsorption, Lead.
_____

INTRODUCTION

High surface area with specific porosity containing activated carbons is extremely versatile adsorbents of major industrial significance. These are used in wide range of applications and commonly used for the removal of species by adsorption from the liquid or gas phase. The number of precursor materials including wood, agricultural wastes, coal and synthetic resins can be able to produce the activated carbon. For the past few decades, researchers have been focused on adsorption technique, which has become the widely accepted method for the removal of contaminants from waste water. Activated carbon adsorption has been cited by the US Environmental Protection Agency (USEPA) as one the best available environmental pollution control technologies [1]. One of the major challenges associated with adsorption using activated carbon is the cost effectiveness. Some researchers have mainly focused on the preparation of the activated carbon from agricultural waste materials as an alternative for the commercial activated carbon. Activated carbons with highly efficient surface properties and specific functionalities can be developed to show high affinity for the adsorption performance [2]. So recently activated carbons were prepared by using bio-waste materials collected from agricultural field [3]. These activated carbons with sufficient no. of pores are very much beneficial for the enhancement of solute adsorption. In this study activated carbon derived from *Brassica juncea* by chemical process is analysed with various techniques such as SEM (Scanning Electron Microscopy) and FTIR (Fourier transmission Infrared Spectroscopy) in order to understand the properties. The objective of this paper is to study the physico -chemical characteristics of activated carbon from *Brassica juncea* with a view to use them in the treatment of ground water near Industrial area.

It belongs to the family of Brassicaceae, commonly known as Indian mustard. It is a perennial herb, usually grown as an annual or biennial, up to 1 m or more tall; branches long, erect or patent; lower leaves petioled, green, sometimes with a whitish bloom, ovate to obovate, variously lobed with toothed, scalloped or frilled edges, lyrate-pinnatisect, with 1–2 lobes or leaflets on each side and a larger sparsely setose, terminal lobe; upper leaves subentire, short petioled, 30–60 mm long, 2–3.5 mm wide, constricted at intervals, sessile, attenuate into a tapering, seedless, short beak 5–10 mm long. The principal growing countries are Bangladesh, Central Africa, China, India, Japan, Nepal, and Pakistan, as well as southern Russia north of the Caspian Sea. Young tender leaves of mustard greens are used in salads or mixed with other salad greens. Older leaves with stems may be eaten fresh, canned or frozen, for pot herbs, and to a limited extent in salads. Mustard greens are often cooked with ham or salt pork, and may be used in soups and stews. Although widely and extensively grown as a vegetable, it is being grown more for its seeds which yield an essential oil and condiment.

MATERIALS AND METHODS

Preparation of activated carbon: Raw bio-adsorbent leaves of *Brassica juncea* (Indian mustard) were collected from nearby areas. They were dried in open air and powdered. The homogenous powder was used for experiments. Activated carbon of the biomaterial was prepared by treating with concentrated sulphuric acid (Sp. gravity 1.84) in a weight ratio of 2: 1 (biomaterial: acid). In order to have sufficient quantity of carbon for systematic studies, 400g of the powdered leaves were carbonized using about 109 mL of concentrated sulphuric acid in each instance. The mixing of sulphuric acid and the powdered leaves was done by adding 30 mL portion of the acid to the powdered leaves rinsing it three times taken in a 1000 mL beaker with stirring. Care was taken for the acid not to burn the biomaterial and the oxidation process is complete. The resulting black product was kept in air-free oven monitored at 195°±5°C for 3h followed by washing with distilled water several times until free excess acid is removed and dried at $105^{o} \pm 5^{o}$C. The activated carbon obtained from biomaterial was ground and the portion retained between 90 and a 125 μm sieve was used for the metal adsorption experiments [4, 5]. Those in size ranges greater than 125 μm were carefully ground and sieved to the desired range. The final material in the size range 90-125 μm, were characterized

and preserved for further experimental studies. The yield was about 40 % relative to the starting precursor.

Characterization of the activated carbon [6-9]: Characterization of activated carbon from *Brassica juncea* (ACBJ) was studied by all parameters like moisture, ash content, matter soluble in water and acid, pH of the carbon (water extract), phenol number, methylene blue value, iron content and ion exchange capacity etc. The studies of FTIR spectra and SEM images show various important functional groups and surface morphology, which are mainly responsible for heavy metals binding.

Chemicals: All chemicals and reagents used were of analytical grade. The pH values of the solutions were measured by digital pH meter. Dilute solutions of HCl and NaOH were used for adjustment of pH from 2–10. All the working solutions were prepared and diluting with deionized water.

Adsorption studies: The batch experiments were performed by adding desired amount of the metal solution in 250 mL of beaker at desired adsorbent dose, pH and temperature. The solution was transferred in to column for a definite period. Adsorbent dose, temperature and pH were optimized by varying one variable at a time (OVAT). After equilibrium the system was allowed to settle for 20-30 min and eluted the column with water for the un-exchanged ions. The pH of the original solution and the eluted solution was measured using Systronics digital pH meter type LI-120. The difference in the ion concentration before and after adsorption experiments represents the amount of the metal ions adsorbed. All experiments were performed at room temperature (25°C±2°C). The free ion concentrations of all the ions in test solution were measured by atomic absorption spectrometer-SVL spectronics-205 model.

The percent removal of metal ions was calculated by using the formula-

$$\% \text{ removal} = \frac{C_i - C_f}{C_i} \times 100$$

Where, Ci= initial concentration, Cf= final concentration

RESULTS AND DISCUSSION

The created porosity on the surface of carbon and the ion exchange capacity value which is found to be 1.12 meq g^{-1} indicates the possible removable of certain inorganics from aqueous solution. Table 1 show the matter soluble in acid and water are comparable for the activated carbon, phenol number and

Table 1. Properties of activated carbon prepared from *Brassica juncea* (ACBJ)

Property of activated carbon	Value of each parameter
Moisture content	6.90 %
Ash content	37.50 %
Total carbon	64.45 %
Apparent density	0.46 g mL^{-1}
Matter soluble in water	0.13 %
Matter soluble in acid	0.16 %
pH of the carbon (water extract)	3.62
Ion exchange capacity	1.12 meq g^{-1}
Methylene blue value	15.0 mg g^{-1}
Phenol number	76.00 mg g^{-1}
Iron	0.07 %
Calcium oxide (from ash)	5.02 %
Magnesium oxide (from ash)	0.11 %
Sodium oxide (from ash)	0.12%
Potassium oxide (from ash)	0.03%

methylene blue value were found to be 76.0 mg g^{-1} and 15 mg g^{-1}, which suggest that ACBJ was suitable for inorganic adsorption. The pH of ACBJ, found to be 3.62 suggests that the carbon is acidic in nature and the fixed carbon content is 37.50%. Therefore, ACBJ possesses reasonable bulk density, ion exchange capacity and higher surface area, which makes it to be successfully employed for the removal of inorganics [**10, 11**].

FTIR Spectra of ACBJ: FTIR spectrum of activated carbon of *Brassica juncea* (ACBJ) is shown in figure 1. The spectrum displays a number of absorption peaks, indicating the complex nature of the material examined. O-H, O=C-, -COOH and SO$_3$H groups are the main functional groups of ACBJ that participate in metal binding [**12**]. The absorption bands at 3854.36 cm^{-1} due to the stretching vibration of free O-H from water and 3401.15 cm^{-1} is stretching vibration of O-H from carbon matrix. A peak at 2362.07 cm^{-1} indicates stretching vibration of O=C=O. The peak observed at 1577.93 cm^{-1} can be assigned to stretching vibration of O=C-, for carboxylate ions. Strong peaks at 1162.17 cm^{-1} and 1122.18 cm^{-1} are due to the presence of SO$_2$ and S=O groups which favour ion exchange mechanism [**13, 14**]. The peak at 677.20 cm^{-1} is due to C-S stretching vibration and peak at 614.26 cm^{-1} is due to C-C bending while peak at 594.53 cm^{-1} is due to O-H bending. It was reported in the literature [**15, 16**] that the carboxylic groups of biomaterials are mainly responsible for heavy metals binding.
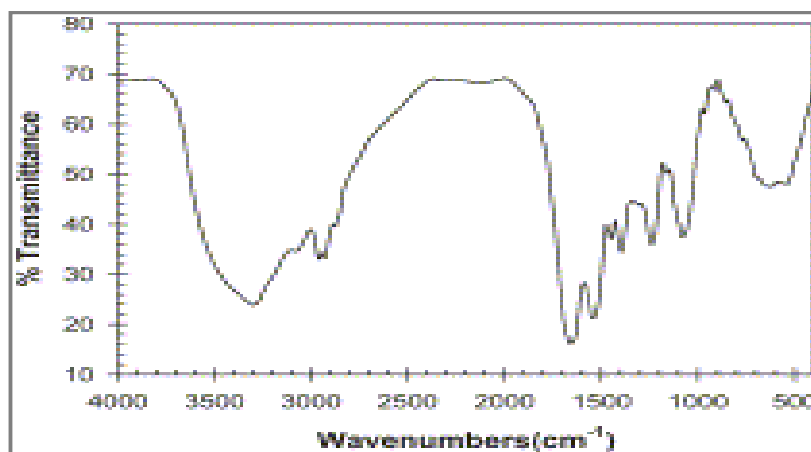

Figure 1. FTIR Spectrum of ACBJ.

SEM: SEM images presented in figure 2 shows the structure of ACBJ in low and high magnifying conditions respectively. Further, it shows the irregular surface, bigger holes and caves type of openings on the surface. The indication of porous nature is responsible for favorable adsorption. Such type of structure raises the possibility of metal ions to be adsorbed and trapped (Figure 3).
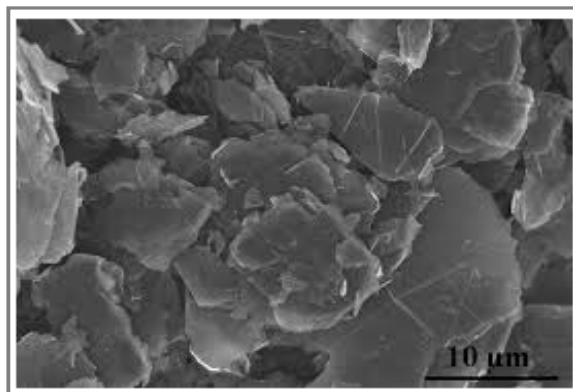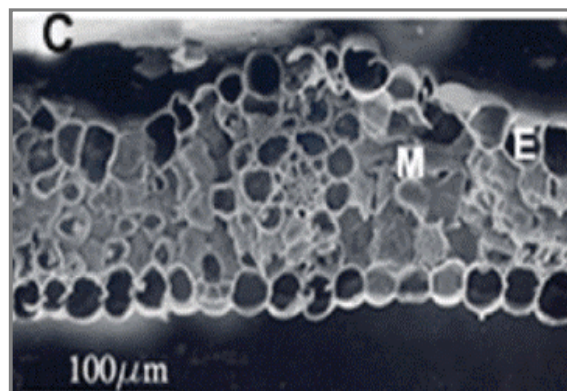

Figure 2. SEM Image of ACBJ (Magnification X50).

E=Epidermal cells, M=Palisade Mesophyll cells, C=Treated leaves
Figure 3. SEM Image of ACBJ (Magnification X2000).

Effect of contact time on adsorption: It is evident from figure 4 that the removal of lead ions increases as contact time increases. Initially, the rate of uptake is fast but, equilibrium was attained in 3 h. With further increase in contact time to 24 h, the percentage adsorption is not affected. Therefore, the contact time can be optimized to 3 h.

Effect of Quantity of Adsorbent on Adsorption: The adsorption of lead ions increased linearly as the amount of adsorbent was increased gradually from 0.25 g to 4.0 g (Figure 5). The maximum adsorption was obtained at adsorbent dose of 4.0 g. Further increase in the quantity of the adsorbent up to 5 g does not affect the adsorption much. About 4.0 g of the adsorbent is sufficient to absorb the maximum ions in the experimental conditions. The increase in the removal efficiency, as adsorbent dose increases, is due to the availability of more adsorbing sites at higher doses. Experimental results are given in table 2.
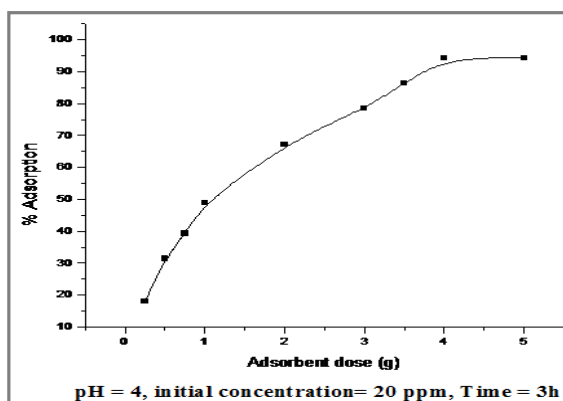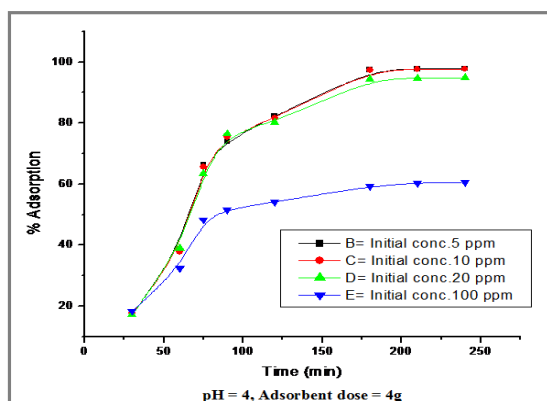
Figure 4. Effect of contact time on adsorption of lead ions	**Figure 5.** Effect of adsorbent dose on adsorption of lead ions.

Table 2. Effect of Adsorbent Dose on Adsorption of Lead Ions

Adsorbent dose (g)	0.25	0.5	0.75	1.0	2.0	3.0	3.5	4.0	5.0
% Adsorption	18.1	31.4	39.3	49.0	67.2	78.4	86.3	94.2	94.3

Effect of initial concentration of lead ions: Removal of Pb(II) from aqueous solution was studied for concentrations ranging from 5 to 100 ppm. The percentage adsorption of Pb(II) at different concentrations at ($25 \pm 2℃$) from 50 mL solution of different initial concentrations (equilibrated with 4.0 g of adsorbent) is shown in figure 6 and table 3. As can be seen from the figure, the removal of metal ion is found to increase with decrease in initial concentration. At the experimental condition of 4.0 g dose of adsorbent and pH adjustment maximum adsorption was obtained for concentrations of 5 and 10 ppm.
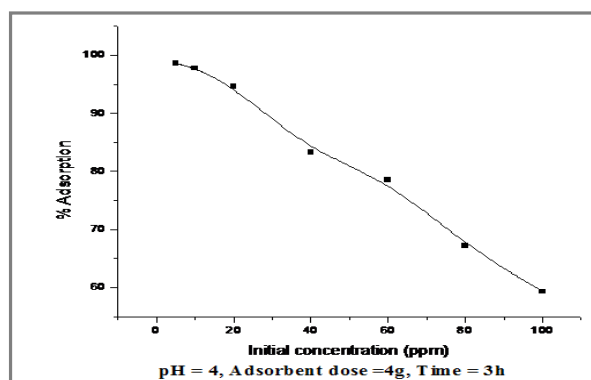

Figure 6. Effect of Initial Concentration on Adsorption of Lead Ions.

Table 3. Effect of Initial Concentration on Adsorption of Lead Ions

Initial concentration (ppm)	5	10	20	40	60	80	100
% Adsorption	98.6	97.8	94.6	83.3	78.5	67.2	59.3

Effect of pH: The adsorption of Pb(II) was obtained maximum at pH 4.0 for both 10 and 50 ppm. as shown in Fig.7.At pH < 2.5, H^+ ions compete with Pb(II) ions for the surface of the adsorbent which would hinder Pb(II) ions from reaching the binding sites of the sorbent caused by the repulsive forces. At pH > 6.0, the Pb(II) gets precipitated as lead hydroxide. For this reason, the maximum pH value was selected to be 4.0 (Figure 7). The highest efficiency was 97.5% at a pH of 4.0 for 10 ppm and 80.2% for 50 ppm. At low pH, there is a decrease in the removal of Pb(II) due to higher concentration of H^+ ions present in the aqueous medium which compete with M+ ions for the surface adsorbing sites[17].A change in the pH of the solution was observed after adsorption had taken place. In all the cases the pH of the solution decreased after equilibrium was achieved. The change in pH was dependent on the amount of adsorbent dose. The higher the adsorbent dose the larger the change in pH. Adsorption of the metal ions on the surface could result in the release of more H^+ ions from the surface, which suggests ion exchange mechanism. The adsorption of lead ions at lower pH, was also observed in other bio-materials [13, 14] and similar mechanisms were suggested by other researchers [15].
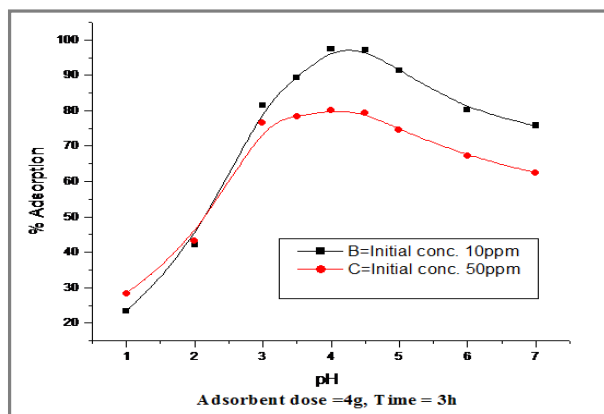

Figure 7. Effect of pH on adsorption of Lead ions.

Adsorption Isotherm: Adsorption isotherm indicates how molecules of adsorbate distribute between the solid and liquid phase when the adsorption process reaches an equilibrium state [18]. Batch adsorption experiments resulted in points of the adsorption isotherm, which was approximated by the Langmuir model.

$$q = \frac{q_{max}bC_{max}}{1+bC_{eq}} \quad \dots 1$$

where q_{max} is maximum adsorbate uptake and b is the Langmuir constant related to energy of adsorption, which quantitatively reflects the affinity between the adsorbent and the adsorbate. The q was evaluated according to Eq 2

$$q = \frac{V(C_i - C_{eq})}{m} \quad \dots 2$$

where V is the volume, C_i and C_{eq} are the initial and the unadsorbed concentrations of the metal ion at equilibrium, and m is mass of the biomaterial. The Langmuir parameters were obtained by fitting the experimental data to linearized equation (3) derived from Equation 1.

$$^1/q = \frac{1}{q_{max}} + \frac{1}{C_{eq}\, q_{max}\, b} \quad \ldots 3$$

The Freundlich isotherm (4) can be derived from the Langmuir isotherm by assuming that there exists a distribution of sites on the adsorbent that have different affinities for different adsorbates with each site behaving according to the Langmuir isotherm.

$$q = KC^{1/n} \quad \ldots 4$$

Where K is the measure of the capacity of the adsorbent (mass of adsorbate/mass of adsorbent) and n is a measure of how affinity for the adsorbate changes with changes in adsorption density. n > 1 indicates the affinities decrease with increasing adsorption density. Evaluation of the K and n can be accomplished using the linearized form equation 5 of equation 4.

$$\log q = \log K + \frac{1}{n}\log C \quad \ldots 5$$

From the values obtained for these parameters, the theoretical Freundlich curves were calculated and plotted in figure 8. It can be observed that experimental data fit isotherm adequately. The Freundlich parameters [19] as well as the correlation coefficient are listed in table 4. The applicability of the Freundlich model to the experimental data indicates monolayer coverage on heterogeneous adsorbent surface by each of lead(II) ions. For comparison, the Langmuir adsorption isotherm [20] is also given in figure 9.

Table 4. Freundlich Isotherm Parameters

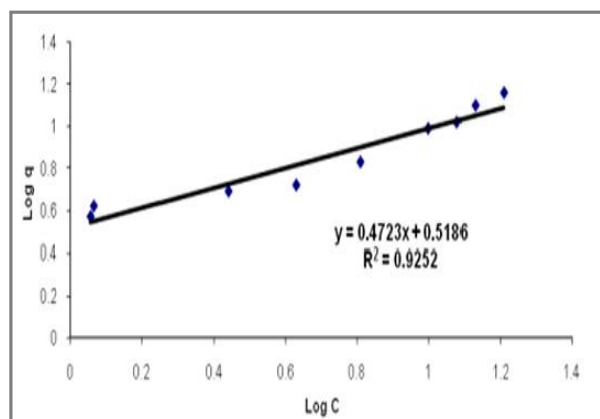| Equation	K (mg g^{-1})	n	R^2
log q=0.4723logC+0.5186	3.3	2.12	0.92

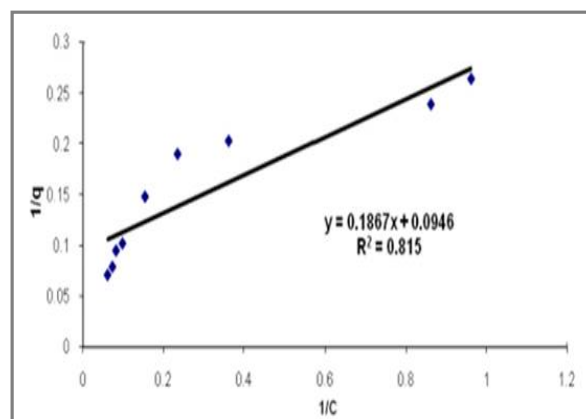**Figure 8.** Freundlich adsorption isotherm of lead ion.   **Figure 9.** Langmuir adsorption isotherm lead ion.

Removal of Pb(II) from ground water near industrial area: Results of the studies show the activeness of the activated carbon from *Brassica juncea*. Therefore, it was applied to remove Pb(II) from ground water samples near industrial area. Nearly five water samples were collected in to the sampling bottles from different places of industrial area, Srikakulam. Initially sampling bottles were washed with distilled water thoroughly and then dried. At the collection point, containers were rinsed with samples 3 times and then filled with sample, corked tightly, and taken to the laboratory for treatment and analysis. The batch experiments were performed by taking samples in 250 mL of beaker at desired adsorbent dose, pH, time and temperature as described earlier. The percent removal of Pb from the samples by adsorption is 97. 5%. The difference of Pb (II) concentration before and after

adsorption experiments were measured by atomic absorption spectrometer-SVL spectronics-205 model. The results were shown in table 5.

Table 5. S1–S5, Lead contaminated Ground water Samples

Sample	Concentration of Pb (II) mg L^{-1}		% adsorption
	Initial	Final	
S1	5.0	0.1250	97.5
S2	5.1	0.1376	97.3
S3	5.0	0.1250	97.5
S4	5.5	0.1979	96.4
S5	5.2	0.1559	97.0

APPLICATION

The prepared activated carbon is eco-friendly and low cost. This method is applicable to remove lead (II) from water nearby Industrial areas.

CONCLUSION

The present investigation showed that activated carbon derived from *Brassica juncea* is effective for the removal of lead (II) from ground water near industries. FTIR data and SEM images showed that main functional groups of ACBJ are O-H, O=C-, -COOH and SO_3H, that participate in metal binding and also the irregular surface, bigger holes and caves type of openings on the surface respectively. This indication of porous nature is responsible for favorable adsorption. Such type of structure raises the possibility of metal ions to be adsorbed and trapped. Batch adsorption experiment showed that Pb (II) ion adsorption properties are great dependence on pH, time and metal ion concentration. The amount of adsorption increased with increase in pH from 1.0 to 7.0. The optimum pH for the uptake of lead adsorption on the adsorbents is 4. Adsorption equilibrium for the metal was reached in about 3 h. In this study, the removal of Pb(II) is 97.5 % by adsorption under the conditions employed with an effective dose of 4.0 g of adsorbent. Experimental results are in good agreement with Freundlich adsorption isotherm model, and have shown a better fitting to the experimental data. Based on this study, it was observed the adsorbent is effective for the removal of Pb(II) from the ground water samples near industrial area.

REFERENCES

[1]. J. B. Martin (USEPA) Federal Register, **2012**, 77, 58.

[2]. R. Manual Fernado, F. PeriraSamanta, J. M. O. Soares Jose, L. R. Fao Jose, A. Figureueiredo carbon, **2003**, 41, 811

[3]. M. Nageswara Rao, Y. Hanumantha Rao, Ch. Chakrapani, Ch. Suresh Babu, B. V. Rajeswara Reddy, P. Haritha and Kaza Somasekhara Rao, adsorption studies of methylene blue dye using prepared low-cost activated Kaza's Carbons, *J. Chem. Pharm. Res.*, **2011**, 3(5), 363.

[4]. F. Derbyshire, M. Jagtoyen, M. Thwaites, Activated Carbon Production and Application. In Porosity in Carbon, Patric, J. W., ed., John Wiley and Sons Inc: London, **1995**.

[5]. F. Rodriquez Reinoso, Production and Application of Activated Carbon. Hand Book of Porous Solids, Wiley, VCH, **2002**.

[6]. ISI, Methods of sampling and test for activated carbon used for decolorizingvegetable oils and sugar solutions. USA, **1977**.

[7]. Annual book of ASTM standards, section 15, West Conshohocken, PA, USA, **1999**.

[8]. A. Jain, K. Suhas, S. Jain., A. Bhatnagar, *Toxicol. Environ. Chem.*, **2001**, 84, 41.

[9]. A. Jain, K.Suhas, and A. Bhatnagr, Methylphenols Removal from Water by Low-Cost Adsorbents, *J. Colloid interface. Sci.*, **2002**, 251, 39

[10]. N. Verheyen, R. Rathbone, M. Jagtoyen, F. Derbyshire, *Carbon*, **1995**, 33, 763.

[11]. H. Teng, S. C. Wang, *Carbon*, 2001, 39, 755.

[12]. E. Malkoc, Y. Nuhoglu, Removal of Ni(II) ions from aqueous solutions using waste of tea factory: Adsorption on a fixed-bed column, *J. Hazard. Mat*., **2006**,135, 328.

[13]. H. Kaur, Spectroscopy, Prakashan Publication, Meerut, India, **2001**.

[14]. A. Kanan, S. Thambidura, EJEAFche, **2007**, 6, 1803.

[15]. K. H. Chong, B. Volysky, Metal biosorption equilibria in a ternary system, *Biotechnol. Bioeng.*, **1996**, 49, 629.

[16]. W. Gerald, E. Strandger, I. Startiling, J. R. Schumate, J. R. Parrott, *Appl. Environ. Microbiol.* **1981**, 49, 629.

[17]. T. K. Naiyaa, A. K. Bhattacharya, S. Mandalb, S. K. Das, The sorption of lead(II) ions on rice husk ash, *J. Hazardous Materials*, **2009**, 163, 1254.

[18]. K. Li, Z. Zheng, Ye, Li, Characterization and lead adsorption properties of activated carbons prepared from cotton stalk by one-step H3PO4 activation, *J. Hazardous Materials*, **2010**, 181, 440.

[19]. A A.Chakravarty, A.Mohanty, T.N.Sudha, A.K.Upadhyaya, J.Konar, J.K.Sirkar, A.Madhukar, K.K.Gupta, Removal of Pb(II) ions from aqueous solution by adsorption using bael leaves (Aegle marmelos), *J. Hazardous Materials*, **2010**, 173 , 502

[20]. Y. Li,Q, Du, X. Wang, P .Zhang, D. Wnag, Z. Wang, Y. Xia, Removal of lead from aqueous solution by activated carbon prepared from Enteromorpha prolifera by zinc chloride activation, *J. Hazardous Materials*, **2010**, 183, 583.