International Journal of Research in Advent Technology, Vol.6, No.12, December 2018
E-ISSN: 2321-9637
Available online at www.ijrat.org

A Study on the Environmental Applications of Activated Carbon and Its Polymer Composite from Agro Waste Materials

*Aswini K, Jaisankar V**
PG and Research Department of chemistry,
Presidency College (Autonomous), Chennai-600 005, Tamil Nadu, India
**Corresponding author: vjaisankar@gmail.com*

Abstract- In recent years, pollution due to heavy metals creates serious hazard to environment which is a matter of serious concern. The effluents from industries containing heavy metals are one of the major environmental problems in the world. In this investigation, adsorption of heavy metals such as Copper, Cadmium and Lead using sugarcane bagasse and its polymeric composite has been investigated was studied. A low-cost activated carbon (SBAC) prepared from sugarcane bagasse via carbonisation followed by chemical activation treatment process. The performance analysis was carried out as a function of various operating parameters such as initial concentration of metal ion, adsorbent dosage, contact time and pH. The performance analysis revealed that there is a significant percentage removal of metal was achievable by this method. The activated carbon and the composites of (PVP/SBAC), (PEG/SBAC) and (PVA/SBAC) were characterized by Fourier transform infrared (FTIR) and X-ray Diffraction Analysis (XRD). The pore structure was evaluated through morphology analysis using high resolution scanning electron microscope (HRSEM).Also Langmuir, Freundlich and Temkin models were used to analyse the adsorption equilibrium.

Keywords: Sugarcane bagasse; activated carbon; polymer composite; blending technique; Adsorption Isotherms.

1. INTRODUCTION

In water treatment, the most widely used process is adsorption on the surface activated carbon which can remove organic as well as inorganic compound at very low concentration due to the following factors, (1) relatively easy (2) safer to operate (3) can be used both in batch and continuous equipment (4) does not form sludge and (5) can be carried out using regenerated adsorbents. Despite its frequent use in the water and waste industries activated carbon remains an expensive material. In view of high cost and tedious procedures for preparation of activated carbon, there is a continuous research for low cost potential carbon.

Among heavy metals in waste water Pb, Cu and Cd are considered for high priority due to their toxicity and high disposal rate. Lead causes many serious disorders like, anemia, kidney disease, nervous disorders, and even death; it heads the toxic element list [6]. One of the conventional adsorbent, activated carbon has been extensively used in many applications. However, the high cost effectiveness of activation processes limits its usage in wastewater treatment processes [7]. The present research activity aims toward contributing in the search for cost effective or low cost adsorbents of natural origin and their applicability in recovery as well as removal of heavy metals from the industrial wastewater.

The objective of the present work is to investigate the biosorption potential of sugarcane bagasse in the removal of Pb(II), Cu(II) and Cd(II) metal ions from aqueous solution[8]. Optimum biosorption conditions were determined as a function of pH, biomass dosage, contact time, and temperature. The Langmuir, Freundlich and Timken models were used to describe equilibrium isotherms [9-10]. Also, the adsorption behavior of SBAC/polymer composites using various polymers such as Polyvinylpyrrolidone (PVP), Polyethyleneglycol (PEG) and Polyvinylalcohol (PVA) were investigated and compared.

2. Materials

The materials used for the preparation of simulated wastewater were Copper Nitrate, Lead Nitrate and Cadmium Nitrate purchased from Merck, was of purity 98-99%.The H_3PO_4 HCl and NaOH All other chemicals used were analytical grade and used as such. The Sugarcane bagasse collected from agriculture waste.

3. Experimental

3.1. Preparation of activated carbon from sugarcane bagasse (SBAC)

Sugarcane bagasse is a type of agricultural waste (agro waste). After juice was extracted, the remaining fiber was taken. The fiber was crushed and ground well in order to produce powder. It was washed repeatedly in tap water and distilled water thoroughly to remove dust and other impurities and then dried in oven at 100±5°C for 24 hours. It was later crushed to smaller size to ensure uniform impregnation with the activating agent. It was then treated with 3M phosphoric acid at 80°C for 3 hours. The pre-treated sugarcane bagasse was washed thoroughly and dried air oven at 100±5°C for 24 hours. The treated sugarcane bagasse is a carbonized at 450°C for 2 hours. Sugarcane bagasse Activated Carbon (SBAC) obtained was stored in an air tight container. The process was repeated to collect the substantial amount of activated carbon.

3.2. Preparation of polymer composites (PVP/SBAC, PEG/SBAC and PVA/SBAC)

The powdered SBAC was treated with an emulsion of readily available synthetic polymer-PVP. Nine parts by weight of activated carbon obtained from the stem of Sugarcane bagasse were mixed with one part by weight of PVP to form a semisolid mass. The agglomerated product was dried and ground into fine powder. The adsorbent was dried at 110^0C for 2 hours. This powder was then used as an adsorbing material. As mentioned above the other polymer composites are prepared using PEG and PVA and named as PEG/SBAC and PVA/SBAC respectively. [11]

3.3. Preparation of simulated wastewater

The 1000 ppm standard solution of Copper, Cadmium and lead were prepared by dissolving measured quantities of their respective salts in distilled water. The simulated wastewater was prepared by using measured amount of standard solutions. The concentration of Pb, Cu and Cd was 5ppm, 20 ppm and 15 ppm respectively.

3.4. Adsorption experiment

Adsorption experiment was carried out by measuring 25mL of the simulated wastewater sample and poured into a 100 mL conical flask. 0.6 g of the synthesized SBAC, PVP/SBAC, PEG/SBAC and PVA/SBAC composites were added to different conical flask containing 25mL of wastewater. The conical flask containing the adsorbent and the simulated wastewater was placed on a rotary shaker and shook at 120 rpm at a room temperature of (32^oC) for a period of 150 min to ensure equilibrium. The suspension was filtered using Whatman No.1 filter paper. The concentration of remaining metal ions in the adsorption medium was determined by UV-Visible spectrophotometer [12].

The metal concentration (mg/g) keep possession of the adsorbent phase (*qe*) and the removal efficiency (%) of the adsorbent preparations was calculated using the following equations respectively:

$$q_e = \frac{(C_0 - C_e)v}{w}$$ ------------- (1)

Removal efficiency (%) $= \frac{C_0 - C_e}{C_0} \times 100$--------------- (2)

Where *Co* and *Ce* are the concentrations (mg/l) of metals ions before and after adsorption respectively, *V* (ml) is the volume of the metal ions and *w* (g) is the mass of the adsorbent.

3.4.1. Effect of contact time:

To study the effect of contact time 0.2 gram of adsorbent is taken in 25ml of aqueous solution of initial metal ion concentration 20, 10, 5 mg/ L, at the shaking was provided for 30 minutes. The experiment was repeated for different time intervals like 30, 60, 90, 120, 150 minutes at constant agitation speed 120 rpm, after each interval of time the sample was filtered and was analyzed for determination of optimum contact time.

3.4.2. Effect of adsorbent dose:

The effect of adsorbent dosage on the amount of metal ion adsorbed was obtained by agitating 25ml of metal ion solution of 20, 10, 5mg/ L, separately with 0.2, 0.4, 0.6, 0.8 and 1.0 grams of adsorbent at room temperature for optimum shaking time at constant agitation speed. The filtered solution of metal was analyzed with the help of by UV-Visible spectrophotometer.

3.4.3. *Effect of pH:*

The effect of pH the stock solutions of concentration 20, 10, 5mg/ L, was treated with dilute acid in order to maintain the pH value to 2, 4, 6 and base was added to maintain the pH up to 10. The acid used was freshly prepared HCl and base was NaOH. After setting the pH of the ranges 2, 4, 6, 8 and 10 in different flasks, 25ml stock solution and 0.2 g SBAC, PVP/SBAC, PEG/SBAC and PVA/SBAC was added into each conical flask and allowed to undergo shaking for 150 min. The filtered solution of Metal ion was analyzed with the help of by UV-Visible spectrophotometer.

4. CHARACTERISATION METHODS

The preparation of Activated carbon from Sugarcane bagasse (SBAC) and PVP/SBAC, PEG/SBAC and PVA/SBAC composites were characterized by Spectral methods. A principle of FT-IR spectrophotometry is it relies on the fact that the most molecules absorb light in the infra-red region of the electromagnetic spectrum. X-ray diffraction patterns were collected from 10° to 60° in 2θ by a XRD with CuKα (λ = 0.1542 nm) radiation on a D8 Advance (Bruker-AXS) diffract meter. Surface morphology of samples was analyzed by scanning electron microscope (HR-SEM, S2600 HITACHI).UV/Visible Scanning Spectrophotometer SHIMADZU 1800 using pure components or mixture of components can be used as standard samples.

5. RESULT AND DISSCUSSION

5.1 Fourier Transform Infrared (FTIR) Spectroscopy

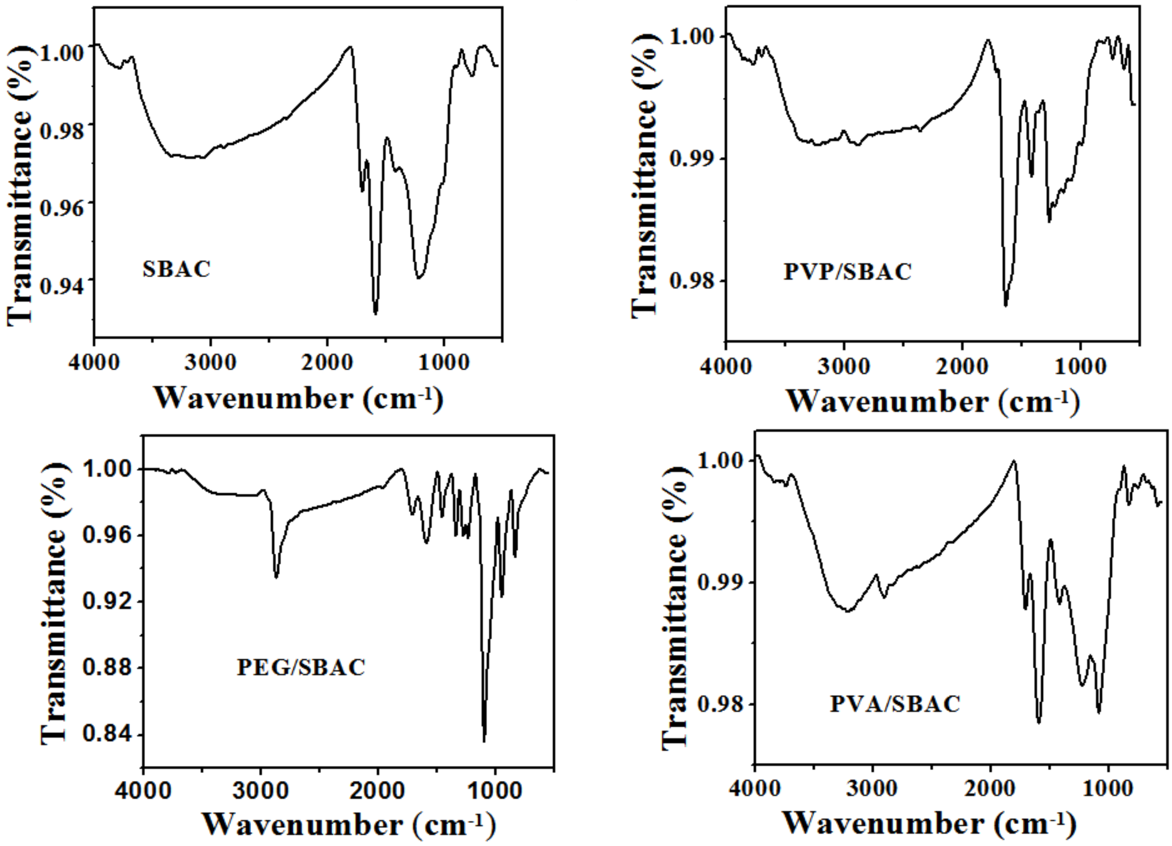


Fig.1 FT-IR spectra recorded for (a) SBAC, (b) PVP/SBAC, (c) PEG/SBAC and (d) PVA/SBAC polymer Composites

The broad band located at about 3000 – 3600 cm^{-1} is assigned to the O–H stretching vibrations of water absorbed on SBAC and polymer composites. The band at 1621cm^{-1} may be attributed to asymmetric stretching vibration of -COO. The band at 1190 cm^{-1} can be attributed to the C=O stretching vibrations. The band at 894cm^{-1} corresponds to the contribution from C – H bond vibration in aromatic compounds. The band at 1458 cm^{-1} the asymmetric stretching vibration of the CN groups of PVP.The stretching vibratin of C-H all 947 and 2870cm^{-1} corresponding to –CH2 of PEG .The bands of CH-CH2 asymmetric and symmetric stretching found at 2908cm^{-1} and 2849 cm^{-1} respectively. The C-C and C-O stretching vibration is observed at1148 cm^{-1} and 1090cm^{-1} respectively. The stretching of the acetate group of PVA appear at 1715 cm^{-1} corresponds to the C=O.

5.2 X-ray Diffraction Analysis (XRD):

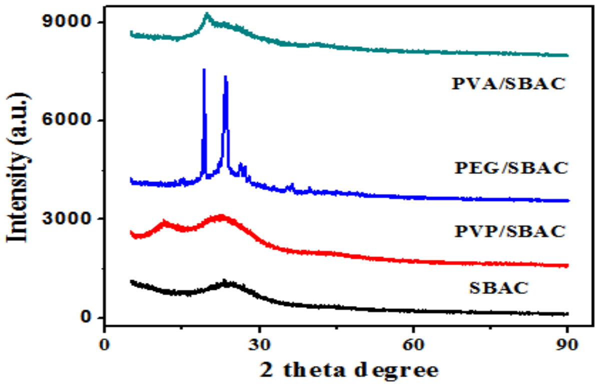


Fig.2. X-ray diffraction pattern of Sugarcane bagasse Activated carbon (SBAC) and PVP/SBAC, PEG/SBAC and PVA/SBAC polymer composites

The XRD pattern showed broad diffraction peak which is centered at 2θ = 23.23^0, 23.13^0, and 19.85^0. This indicates that the activated carbon prepared from Sugarcane bagasse (SBAC) and PVP/SBAC, and PVA/SBAC polymer composites was predominantly amorphous as the existence of broad peaks indicates that the material is amorphous. The degree of crystallinity of polymer was reduced by the addition of amorphous activated carbon. The peaks around 19.24^0, $23.14^0$and 26.35^0 are assigned to PEG crystal, indicating that the crystal structure of PEG is not destroyed.

5.3. High Resolution Scanning Electron Microscopic Analysis (HRSEM)

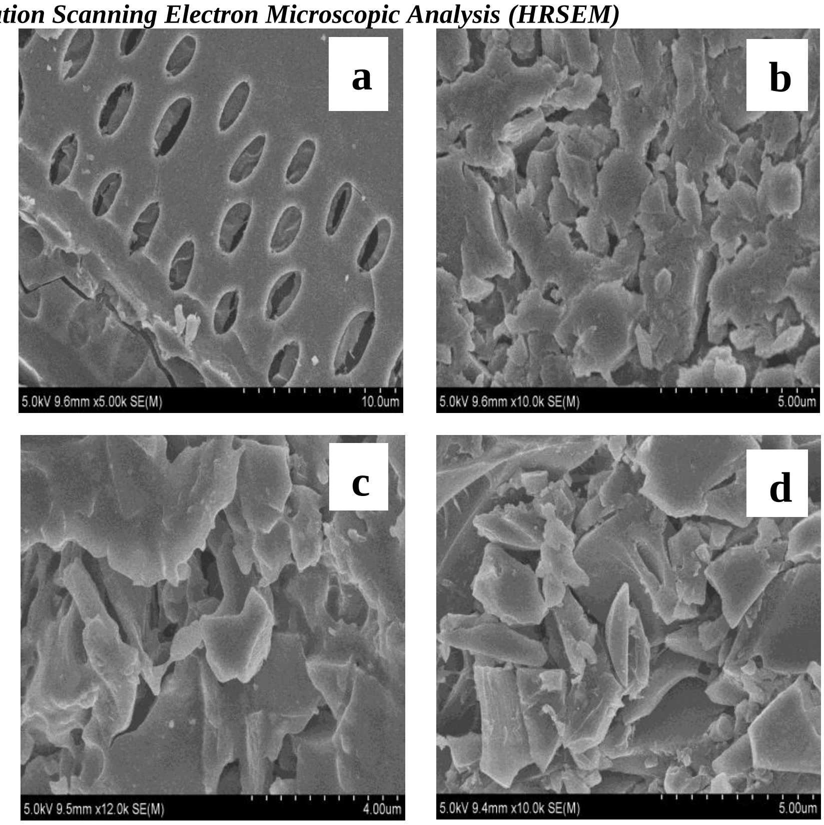


Fig.3. HRSEM images of (a) SBAC, (b) PVP/SBAC, (c) PEG/SBAC and (d) PVA/SBAC polymer Composites

SEM was used to study the morphological features and surface characteristics of the adsorbent study the surface structure of sugarcane bagasse analyzed by scanning electronic microscopy .The SBAC derived activated carbon, PVP/SBAC, PEG/SBAC and PVA/SBAC composites (adsorbent) used in the study for adsorption of metals Fig.3 (a), 3 (b), 3(c) and 3(d) . SEM micrograph for the activated carbon showed that the adsorbent prepared from sugarcane bagasse has a highly porous structure with regular mesoporous. The pores on the surface are clearly identifiable. Figure (a) shows the surface texture of the most efficient prepared activated carbon product. This indicates that the external surfaces of the H_3PO_4 activated carbon have a lot of cavities which are suitable for adsorption to occur.

5.4 Adsorbent method

5.4.1. Effect of contact time:

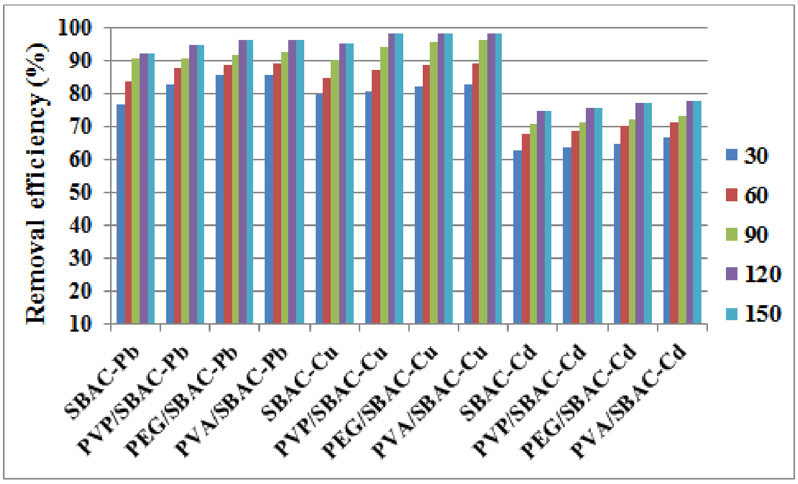


Fig.4. - Effect of Contact time on adsorption of (a) Lead (b) Copper and (c) Cadmium pH=6 (dose= 0.6g)

The SBAC, PVP/SBAC, PEG/SBAC and PVA/SBAC composites as an adsorbent dosage of 0.6 g. The is shown in fig 4.The percentage removal of metal ions approached equilibrium within 120 min of adsorption capacity 92.12%, 94.99%, 96.02%, and 96.39% of lead; Copper 95.37%, 98.11%, 98.24% and 98.38%, and 77.3%, 77.89%, 78.78% and 79.43% for Cadmium removal of metal ions respectively.

5.4.2 Effect of adsorbent dosage:

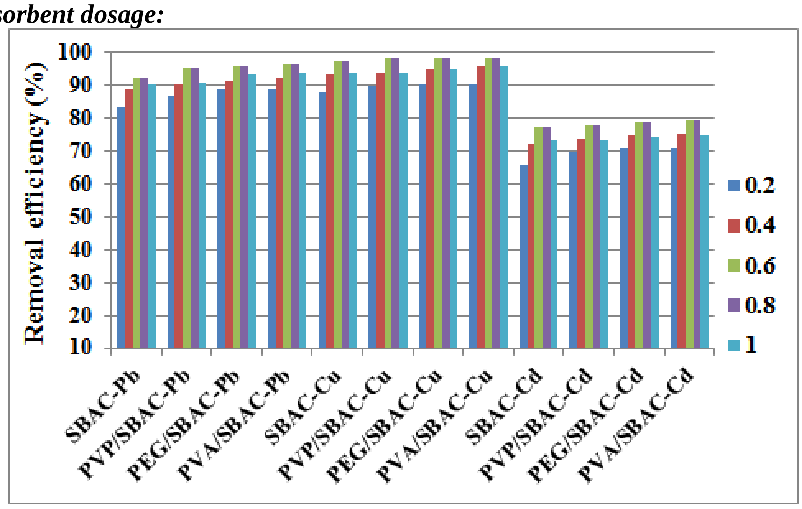


Fig.5. - Effect of Adsorbent dosage on adsorption of (a) Lead, (b) Copper and (c) Cadmium pH=6 (Contact time= 120 min)

The effect of dosage of adsorbent SBAC, PVP/SBAC, PEG/SBAC and PVA/SBAC composites at a Contact time of 120 min is shown in fig 5 .The percentage removal of metal ions approached equilibrium within 0.6 g of adsorption capacity 92.21 % , 95.09%, 96.02% and 94.0896.29 % of lead; Copper 97.09% , 98.29%, 98.52% and 98.54% and 77.3%, 77.89%, 78.78% and 79.43% removal of metal ions respectively, after which further increase in adsorbent dosage, brought no increase in adsorption, which was as a result of overlapping of adsorption sites due to overcrowding of adsorbent particles.

5.4.3 Effect of pH:

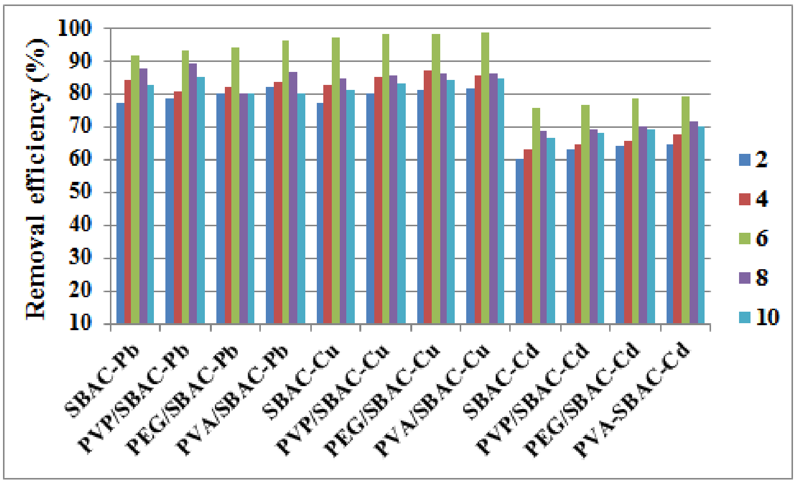


Fig.6.-Effect of pH on adsorption of (a) Lead (b) Copper and(c) Cadmium pH=6 (dose= 0.6g)

The SBAC, PVP/SBAC, PEG/SBAC and PVA/SBAC composites at a Contact time of 120 min with absorbent dosage of 0.6gm at pH 6, shows maximum removal of 91.98 %, 93.45, 94.33 and 96.39% for lead; Copper 97.55%, 98.28%, 98.49%, and 98.72%; 75.9%, 76.87%, 78.55%, and 79.18 for Cadmium respectively. From the results above, it reveals that the adsorption capacity of SBAC, PVP/SBAC, PEG/SBAC and PVA/SBAC depends on the pH of Stimulated waste water. At lower pH values, the large number of H^+ ions neutralizes the negatively charged adsorbent surfaces, thereby reducing the hindrance of the metal ions. At high pH values, the reduction in adsorption may be due to the abundance OH^- ions causes increased hindrance to the diffusion of metal ions. From fig (6) the percentage removal of metal ions increases sharply and attain maximum at pH 6, for SBAC, PVP/SBAC, PEG/SBAC and PVA/SBAC composites. There after the percent removal decreases with increase in pH.

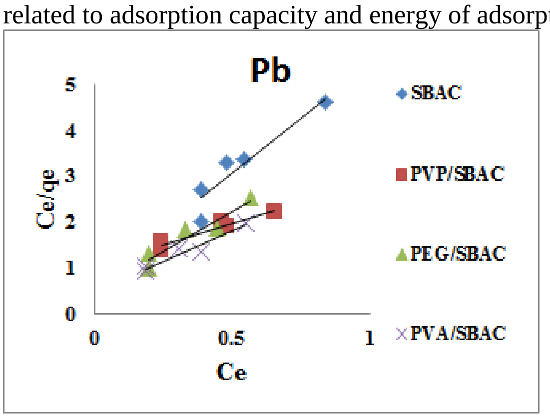
5.5. Adsorption study of Langmuir and Freundlish Isotherm

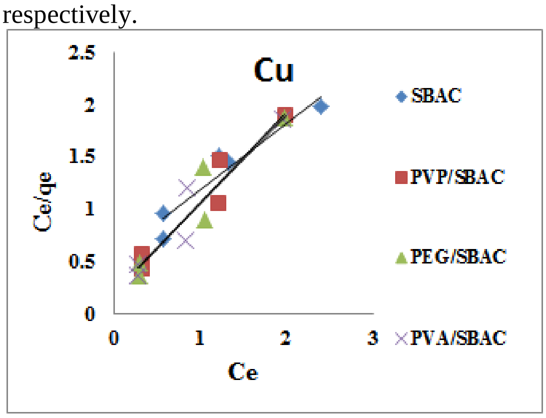
5.5.1. Langmuir adsorption isotherm

The Langmuir equation is derived from simple mass-action kinetic, assuming chemisorption. This model is based on two assumptions that the forces of interaction between adsorbed molecules are negligible and once a molecule occupies a site and no further sorption takes place. The saturation value is reached beyond which no further sorption takes place. The saturation monolayer can then be represented by the expression:

$$Ce/qe = 1/Qmb + Ce/Qm \qquad \text{----------------} \quad (3)$$

Where, Ce is equilibrium concentration (mg/L), qe is the amount adsorbed at equilibrium time per unit adsorbent (g) and Qm and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively.





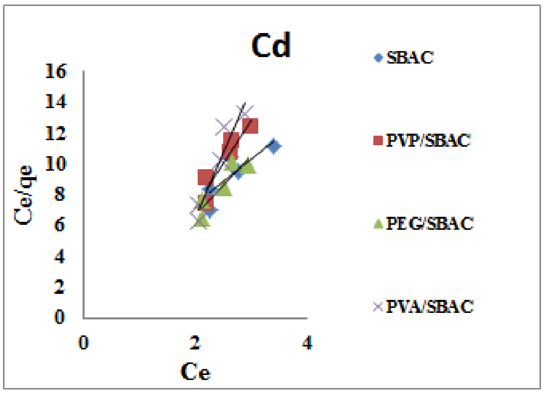


Fig.7. - Langmuir isotherms for the adsorption of removal Pb, Cu and Cd metals with SBAC, PVP/SBAC, PEG/SBAC and PVA/SBAC composites.

Table 1 Langmuir model isotherm parameters for heavy metals Pb, Cu, and Cd.

Adsorbent	Langmuir (Pb)			Langmuir(Cu)			Langmuir(Cd)		
	B value	Qm (mg/g)	R^2	B value	Qm (mg/g)	R^2	B value	Q (mg/g)	R^2
SBAC	7.9254	0.2050	0.8939	1.8505	1.5620	0.916	2.2875	0.3343	0.742
PVP/SBAC	1.7827	0.5403	0.9414	4.3135	1.1756	0.9404	1.4205	0.1798	0.8784
PEG/SBAC	4.1510	0.2887	0.9088	4.6542	1.1453	0.9077	0.2547	0.7970	0.8242
PVA/SBAC	5.2250	0.3817	0.9289	4.9328	1.1434	0.9193	0.9356	0.1320	0.9129

5.5.2. Freundlich adsorption isotherm

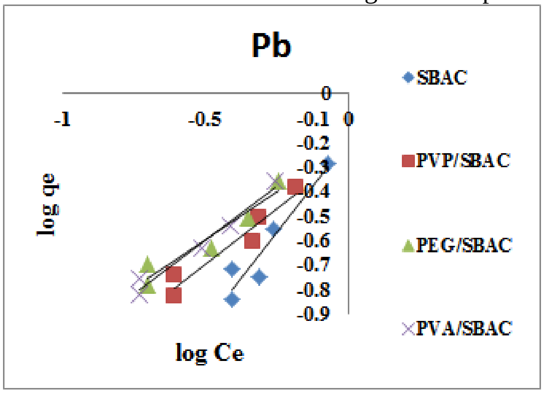
The Freundlich equation is used for heterogeneous surface energies in which the energy term, Qe in the Langmuir equation varies as a function of the surface coverage, qe strictly due to variations in the heat of adsorption:

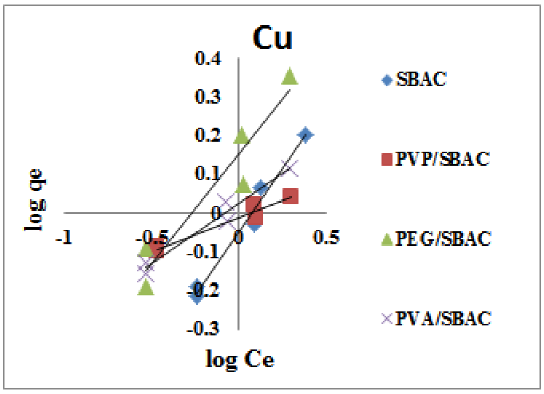
$$qe = kf\ Ce1/n \quad \text{-----------------} \quad (4)$$

The linear form of the equation (5) or the log form is

$$\log qe = \log kf + 1/n \log Ce \quad \text{----------------} \quad (5)$$

kf and n are Freundlich constants; n gives an indication of the favorability and kf the capacity of the adsorbent. Value of n between 1 and 10 indicates good adsorption.





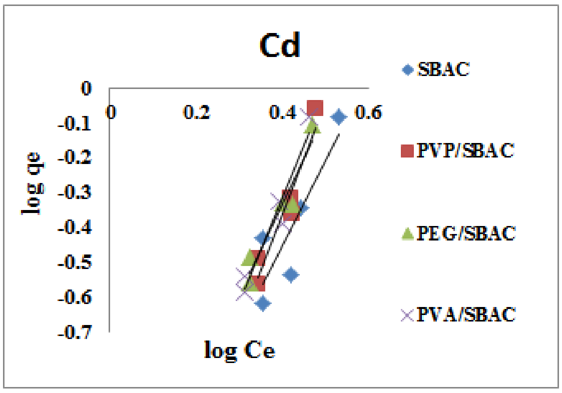


Fig.8. - Freundlich isotherms for the adsorption of removal Pb, Cu and Cd metals with SBAC, PVP/SBAC, PEG/SBAC and PVA/SBAC composites.

Table 2 Freundlish model isotherm parameters for heavy metals Pb, Cu, and Cd.

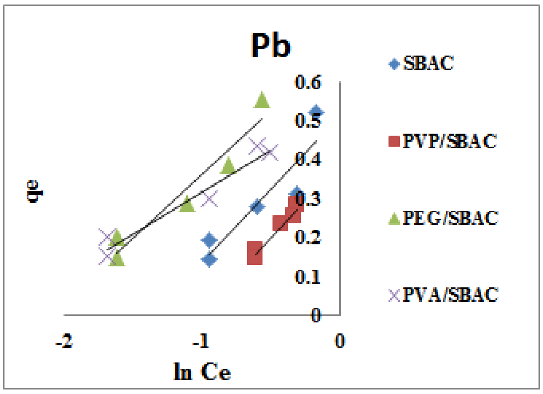
Adsorbent	Freundlich (Pb)			Freundlich (Cu)			Freundlich (Cd)		
	n	K_f (L/mg)	R^2	n	K_f(L/mg)	R^2	n	K_f(L/mg)	R^2
SBAC	1.6595	0.6567	0.908	1.5029	0.8913	0.9776	2.4445	0.0368	0.7532
PVP/SBAC	1.1161	0.5665	0.9328	5.737	0.9723	0.9579	3.2524	0.0216	0.9168
PEG/SBAC	1.2734	0.6220	0.9231	1.7677	1.4142	0.9122	2.6811	0.0723	0.921
PVA/SBAC	1.1287	0.7047	0.9698	3.2123	1.0568	0.9674	3.0029	0.0304	0.9351

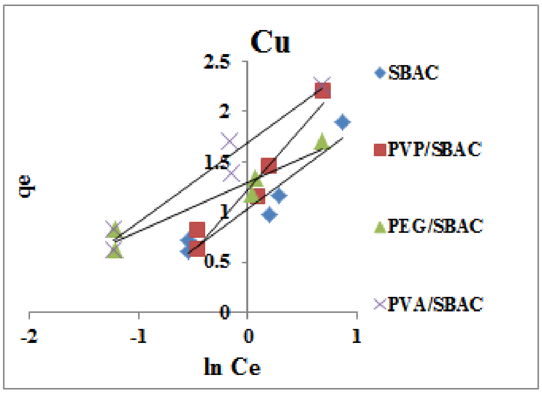
5.5.3. Temkin isotherm model

The Temkin isotherm assumes that the heat of adsorption of all the molecules increases linearly with coverage. The linear form of this isotherm can be given by

qe = (RT/bT) ln (AT) + (RT/bT) ln (Ce) --------------- (6)

q_e is the amount adsorbed at equilibrium in mg/g. b (j/mol), which is Temkin constant related to heat of sorption, A (L/g) Equilibrium binding constant corresponding to the maximum binding energy, R (8.314 J/mol k) Universal; gas constant and T° (K) Absolute solution temperature. The slopes and intercept obtained from the graphical plot q_e against ln C_e were used to calculate the Temkin constants (Table-3).





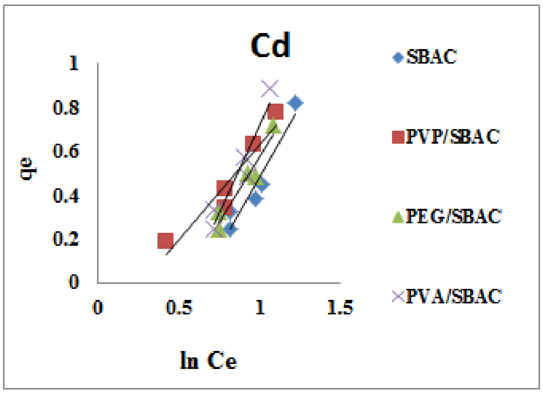


Fig.9. - Temkin isotherms for the adsorption of removal Pb, Cu and Cd metals with SBAC, PVP/SBAC, PEG/SBAC and PVA/SBAC composites.

Table 3 Temkin model isotherm parameters for heavy metals Pb, Cu, and Cd.

Adsorbent	Temkin (Pb)			Temkin (Cu)			Temkin (Cd)		
	bT	AT (L/mg)	R^2	bT	AT (L/mg)	R^2	bT	AT (L/mg)	R^2
SBAC	6662.6342	3.9020	0.8409	3130.9247	3.5834	0.9018	1947.3887	0.5338	0.9264
PVP/SBAC	6529.6579	2.7751	0.9662	2050.1467	2.7169	0.943	2858.7631	0.7555	0.9119
PEG/SBAC	7694.3861	8.0438	0.9305	5146.3575	14.0399	0.9343	2067.2427	0.5918	0.9232
PVA/SBAC	11614.3015	11.8355	0.9494	3159.1949	8.3278	0.9551	1572.3991	0.5748	0.9119

The results of the adsorption of metal ions based on the adsorption models of Langmuir, Freundlich and Temkin show that all equation has a very good correlation coefficient. It indicates the consistency of the results of this research with SBAC, PEG/SBAC and PVA/SBAC Freundlich isotherm but PVP/SBAC is flowed by Langmuir isotherms.

6. CONCLUSION

The Activated carbon from Sugarcane bagasse was successfully prepared and chemically activated using phosphoric acid as activating agent. It was evident from High resolution scanning electron microscopic analysis (HRSEM) that the external surface of prepared material has large cavities and high porosity. Fourier transform infrared spectroscopic (FTIR) and X-ray diffraction analysis (XRD) confirm the chemical and crystalline nature of the prepared Sugarcane bagasse activated carbon (SBAC) and PVP/SBAC, PEG/SBAC and PVA/SBAC polymer composites. The adsorption process obeys SBAC, PEG/SBAC and PVA/SBAC Freundlich isotherm but PVP/SBAC followed by Langmuir isotherm model. The highest adsorption of Copper is determined by 0.6 g and pH = 6. These results suggested that SBAC and its polymer composites can be used as excellent adsorbent materials for removal of heavy metals in wastewater.

ACKNOWLEDGEMENT
The authors sincerely thank the Principal, Presidency College, Chennai, Tamilnadu, for providing access to DST-FIST (SR/FIST/COLLEGE-098/2012) facilities.

REFERENCES

[1] Fierro, V., Torne´-Ferna´ndez, V., Montane´, D., Celzard, A., 2005. "Study of the decomposition of kraft lignin impregnated with orthophosphoric acid". Thermochimica Acta , volume 433, pages 142–148, 2005.

[2] V. Fierro, V. Torne´-Ferna´ndez, A. Celzard. "Kraft lignin as a precursor for microporous activated carbons prepared by impregnation with ortho-phosphoric acid: Synthesis and textural characterization". Microporous and Mesoporous Materials, volume 92 pages 243–250, 2006.

[3] V. Fierro, V. Torné-Fernández, A. "Celzard. Methodical study of the chemical activation of Kraft lignin with KOH and NaOH". Microporous and Mesoporous Materials, volume 101, pages 419–431.2007.

[4] Fierro V., V. Torn´e-Fern´andez, Celzard A. "Highly microporous carbons prepared by activation of kraft lignin with KOH", Studies in Surface Science and Catalysis, volume 160, pages 607–614, 2006.

[5] E. Gonzalez Serrano, T. Cordero, J. Rodriguez-Mirasol, J.J. Rodriguez. "Development of Porosity upon Chemical Activation of Kraft Lignin with $ZnCl_2$". Industrial & Engineering

Chemistry Research, volume 36 (11): 4832-4838, 1997.

[6] C.Karthika,N. Vinnilamani,S. Pattabhi, and M. Sekar. "Utilization of Sago Waste as an Adsorbent for the Removal of Pb(II) from Aqueous Solution: Kinetics and Isotherm Studies". International Journal of Engineering Science and Technology, volume 2 (6), pages 1867–1879, 2010.

[7] H Javadian . "Application of kinetic, isotherm and thermodynamic models for the adsorption of Co (II) ions on polyaniline/polypyrrole copolymer nanofibers from aqueous solution". Journal of Industrial and Engineering Chemistry, volume 20(6): pages 4233-4241, 2014.

[8] BERNARDO, G. R. R.; RENE, R. M. J.; CATALINA,A. T .M. "Chromium (III) uptake by agro-waste biosorbents: chemical characterization, sorption–desorption studies, and mechanism". Journal of Hazardous Materials, volume 170 (2-3), pages 845-854. 2009.

[9] Omar E. Abdel Salam, Neama A. Reiad , Maha M. ElShafei. "A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents". Journal of Advanced Research, volume 2, pages 297–303, 2011.

[10] K. Vasanth Kumar. "Linear and non-linear regression analysis for the sorption kinetics of methylene blue onto activated carbon". Journal of Hazardous Materials. volume 13 (3), pages1538–1544, 2006.

[11] V. Fierro V. Torne -Fernandez D. Montane A. Celzard. "Adsorption of phenol onto activated carbons having different textural and surface properties". Microporous and Mesoporous Materials. volume 111, pages 276–284, 2008.

[12] K. Aswini and Jaisankar V. "Preparation and Characterisation of Activated Carbon from Rice Husk and its Polyvinylpyrrolidone (PVP) Composite for Heavy Metal Removal from Simulated Wastewater". Journal of Water Pollution & Purification Research, volume 4, pages 10-15, 2017.