TECHNIQUE FOR TREATING WASTEWATER WITH LOCALLY MODIFIED ADSORBENT

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ABSTRACT

This work details the techniques for heavy metal removal from wastewater using modified adsorbent. An aqueous wastewater sample at standard atmospheric condition and neutral pH from an oil and gas facility effluent section containing amongst other organic and inorganic contaminants was treated. An adsorbent locally produced in the course of this work from a 2000g of dry empty oil palm bunch (DEOPB), an agricultural waste material obtained from a local oil palm processing mill was used to treat the effluent. The adsorbent was subjected to pyrolysis and chemically activated using a 0.1mol hydrochloric acid (HCl). The adsorption behaviors of iron, copper and cadmium were found to obey Pseudo Second Order kinetic model and the Langmuir isotherm model was used to fit the iron, copper and cadmium adsorption isotherm onto the DEOPB activated carbon with their equilibrium capacities agreeing with experimental data except for the lead component that showed no effect. The heavy metals contaminants investigated using this technique was found to have been removed from the wastewater stream in the following percentage removals; iron; 57%, copper; 99.6% and cadmium; 90% but was ineffective in the removal of the lead component as its concentration remained unchanged throughout the experiment. The locally produced activated carbon was subjected to laboratory analysis and its properties (Density; 0.369g/m³, Particle Size; 0.18mm, Ash Content; 5.73%ww, Porosity; 90%, Surface Area; 691 m²/g) was found to favorably compare with commercial activated carbon.

Key words: biosorbent, kinetics, oil palm bunch, chemical activation

1. INTRODUCTION

The hazardous and non-degradable inorganic compounds present in industrial effluent waste water causes very severe problems to aquatic environment where they are mostly discharged into. These inorganic compounds/heavy metals present in this effluent stream are termed very hazardous because of their high solubility in water and can early be absorbed by living organisms, thereby causing severe and in most cases hereditary diseases in animals Agunwamba, et al (2002). It is with this resolve that various researches are being carried out to investigate the most safe and economically viable techniques in removing these hazardous compounds from Industrial effluent before discharge into water bodies. The effective removal of these metallic compounds from an aquatic environment is still a big problem as most methods/techniques employed in turn create more problems in releasing chemical sludge to the environment.

Adsorption amongst other methods/techniques like co-precipitation, bio-sorption, electro coagulation, ultra-filtration, employed for the treatment and removal of heavy metals from industrial effluent streams have been found to be less expensive and a better alternative in handling these hazardous compounds Salfuddin and Kumaran (2005).

Heavy metals are mostly generated as effluent waste from various industrial activities such as electroplating and metal surfaces treatment, Printed Circuit Board (PCB) manufacturing, wood processing industries, petroleum refining etc. All these industrial activities produce different heavy metals that can be categorized as hazardous waste requiring extensive waste treatment in large quantities of waste waters, residues and sludge (Sorme and Lagerkvist, 2002) and (Kadirvelu et al, 2001)

The conventional methods of heavy metals removal from industrial waste water include many processes such as chemical precipitation, flotation, adsorption, ion exchange and electrochemical desorption. In the recent past chemical precipitation was the most used methods in removing/treating heavy metal laden effluent waste water. Wang et al, 2004 represented the conceptual mechanism for chemical precipitation as:

$$M^{2+} + 2\left(OH^-\right) \leftrightarrow M\left(OH\right)_2 \downarrow$$
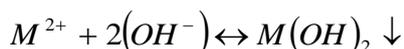
Where M^{2+} and (OH^-) represent the dissolved metals ions and the precipitant respectively, while $M(OH)_2$ is the insoluble metal hydroxide. The adsorbability of a compound increases with: increasing molecular weight, a higher number of functional groups such as double bonds or halogen compounds, increasing polarisability of the molecules (Ujile, 2014). It has also been established that the adsorption force is the sum of all the interactions between all the atoms. The short range and additive nature of these forces results in activated carbon having the strongest physical adsorption forces of any known materials.

Chemical activation method of producing activated carbon involves the addition of substances such as phosphoric acid, zinc chloride, potassium sulphide etc. which restrict the formation of tar to the carbon aqueous material after it is carbonized. Activated carbon via this method has very good adsorption properties and makes use of low temperature, shorter hold times, simplicity and good porous structure when compared to activated carbon obtained via physical activation (Bernado (1997). It is worth noting that chemical activating agents may include phosphoric acid (H_3PO_4), phosphorus pentoxide (P_2O_5), (Izquierdo et al, 2011); zinc chloride ($ZnCl_2$), (Cronje et al, 2011); potassium hydroxide (KOH), (Krol et al, 2011). But for the purpose of this research work, hydrochloric acid (HCl) was used.

The kinetic models have been used to investigate the mechanism of sorption and the potential rate controlling steps, which is an important tool used in selecting optimum operating conditions for full scale batch processes of adsorption. The notable models that have been used are the Pseudo-First order, Psuedo-second order, intra-particle and Langmuir. The removal of Cu (II) ion from aqueous solutions using sago waste as adsorbent, (Aksu and Isoglu, 2005); phenol removal from aqueous systems by tender leaf refuse (Abdelwahad, 2007); Adsorption of Phenol and dye from aqueous solution using chemically modified date peat activated carbon (Ahmedna, 2007); chromium (VI) removal from aqueous solution and industrial waste water by modified date pal trunk (Sunil et al, 2014); amongst other researchers have all applied this various models in their studies Gupta, et al (2001).

Dhiraj et al, (2008) having studied and investigated the conventional techniques for removal of toxic metal contaminants generated from ever growing industrial activities, found that these techniques were not economical as it was too expensive and will further generate huge quantity of toxic chemical sludge.

Toles, et al, (2000) compared the various techniques in modern day heavy metal contaminated effluent waste water treatment at the same water pH and temperature. At the end of their investigation, they were able to state the limitation of the various techniques and came up with the conclusion that the amount of contaminant removal from stream by adsorption was higher making it (adsorption) the most viable of all. They used almond shell for the activation process.

Sandhga et al, (2003), reviewed the technical feasibilities of various low cost adsorbent for removing heavy metal contaminated waste water which included expensive materials like zeolites, chitesan chemical activated carbon and locally made activated carbon. The results obtained were compared with that of chemical activated carbon showed/demonstrated that these low cost materials has high adsorption capacities and remove more heavy metal impurities Babel and Kurniawan (2003); Sud, et al (2008).

Apart from adsorption method using activated carbon adsorbent for removal of heavy metal contaminants from waste water/aqueous solutions, other methods were also investigated. Nural et, al (2014), studied the removal of heavy metals ions from mixed solutions via polymer enhanced ultra-filtration using standard as water soluble bio polymer. It was found at the end of the study that only zinc, Zn (II) and chromium Cr(III) and (IV) gave higher rejection (ie removed by the starch based polymer recovery than lead, (Pb) which was among the contaminants in the stream, thereby making this techniques deficient as compared to adsorption.

Barakat, (2011), was of contrary opinion as to the work done by Nural et al, (2014), in his article, where recent development and technical applicability of various treatment of heavy metals contaminants removal from industrial effluent waste water such adsorption on new adsorbents, electro dialysis photocatalysis, and membrane filtration was reviewed. His work was able to establish that amongst of the mentioned techniques, only adsorption and membrane filtration handled these contaminants optimally.

Activated carbon with surfaces modification was studied and found to be most suitable for the removal of heavy metals from waste water when compared to conventional and expensive methods (Eleni et al, 2015). Other studies were also able to show that surface modification is of great advantage to adsorption process

as it decreases the adsorption equilibrium time (Chingombe, et al, 2005). Adsorption has advantages over other methods for remediation from waste water because its design is simple. It is sludge-free and can be of low capital intensive except that its manufacturing cost is quite high (Pataule, 2005).

Adsorption process reduces energy consumption, increases yield, selectivity, non-generation of toxic sludge etc. It is for these reasons that researchers have gone into these areas with a view to looking at the ways of producing low cost adsorbent. This research work involves developing minimum cost adsorbent obtained from empty dry oil palm bunch (an agricultural waste) and the mass-transfer process involved in removing these metals from process plant effluent.

2. EXPERIMENTAL PROCEDURE

Materials used in carrying out this research work are dry empty oil palm bunch (DEOPB), effluent waste water and industrial chemicals & apparatus such as magnesium oxide (MgO), Hydrochloric acid (HCl), distilled water, methyl blue, litmus papers, cylindrical beakers, laboratory test sieves, crucibles, burners, gas cylinder, locally manufactured pyrolizer, retort stand, analytical weighing balance, atomic adsorption spectrophotometer (AAS), ball roller mill crusher, industrial oven, thermometer, digital weighing balance.

Methods

Experiment was performed to produce carbonaceous materials from dry empty oil palm bunch (DEOPB) using the methods of pyrolysis before activating using HCl and modified with magnesium oxide. The results obtained were analyzed and studied using computer programming software to determine the kinetic parameters.

Sample Collection and Preparation
Empty Palm bunch

Dry empty oil palm bunches were collected in large quantity from a local palm oil processing mill where they (dry empty oil palm bunch) were littered and thus, constituting environment hazards in Obelle community in Emohua local government area in Rivers State. The sample so collected was properly washed, cut into bits and air dried before taking into the laboratory for further processes to obtain the "activated carbon as the adsorbent, this was subjected to chemical treatment with 0.1mol magnesium oxide as the modifier.

Industrial Effluent Waste Water

Waste water sample was collected from one of the major process industries operating in Rivers State and subjected to chemical analysis.

Sample preparation

The air dried empty oil palm bunch cut into bits was pyrolyzed at controlled temperature range 600 to 800°C in the laboratory of the department of Chemical/Petrochemical Engineering Rivers State University of Science and Technology Nkpolu Port Harcourt, for chemical activation and then modified with 0.5mol magnesium oxide (MgO), which was used as the adsorbent.

Production of the Activated Carbon

Production of the activated carbon adsorbent from the dry oil palm bunch was achieved by the pyrolysis method.

Experimental Procedure

A 10gram of the locally produced activated carbon equivalent to 10cm in length was used as the packed bed in the cylindrical beaker as set up in the laboratory. This was then modified with 10ml of 1.0mol magnesium oxide (MgO). A 150mls of the effluent water sample was then poured into the set-up and with the help of the control valve, the AC packed bed and stopper. The sample was able to retain at various times of interest (10mins, 20mins, 30mins, 40mins, 50mins, 60mins & 70mins) with the entire content emptied out with the concentrate collected after each run and replaced with fresh bed of AC.

The results of the various concentrations of the heavy metals of interest (Iron; Fe, Copper; Cu, Cadmium; Cd, and Lead, Pb) in the aqueous effluent sample before and after the treatment with the locally produced activated carbon adsorbent from dry empty oil palm bunch modified with magnesium oxide was determined using an Atomic Absorption spectrophotometer (AAS), model; Analyst 200 and make; Perkins Elmer at various holding time and packed bed length is shown in the Table 1.

Mass transfer model developed from the removal of heavy metal from effluent stream as computed in course of this research (Okwakwam, 2017) is:

$$C_A = C_{Ao}\left[1 - \frac{2\sqrt{D_{AB}t}}{\pi y}\left(1 - e^{-\frac{y^2}{4D_{AB}\,t}}\right)\right] \qquad (1)$$

where C_A, C_{AO}, D_{AB}, y are the concetration of component A at time t (ppm), initial concentration of component A (ppm), mass diffusivity of component A into the adsorbent B (cm/s), mass of adsorbate adsorbed, (g) respectively.

Equation (1) is the model equation describing the concentrations of the heavy metals remaining in the effluent stream after adsorption with time at constant bed height.

The adsorption rate constants for all the metal contaminants were obtained from the expressions Ho and Meckay, (1998) :

$$\frac{1}{q_t} = \frac{1}{K_2 q_e^2 t} + \frac{1}{q_e} \qquad (2)$$

Characterization of Adsorbent

An elementary analysis was performed on the adsorbent thus produced to determine its physical and activity properties, such as bulk-density particle size, surface area, porosity, ash content, hydrogen and sulphur contents. The following values were obtained;

$$Bulk\ Density = \left(\frac{Mass\ of\ Sample}{Volume\ of\ Sample} \right) \qquad (3)$$

$Bulk\ density = 0.369 g/ml$

$$Ash\ content = \frac{(weight\ of\ crucible + sample\ before\ ashing) - (weight\ of\ crucible + sample\ after\ ashing)}{(weight\ of\ crucible + sample\ before\ ashing)} \times 100$$

$$(4)$$

$Ash\ Content = 5.73\%\ w/w$

Particle size: a particle size distribution of 1.18mm to 1.40mm was used for effective adsorption. This was achieved using a "Laboratory Test Sieve, Appeture 1.18/1.40mm, ENDECOTT LTD, London England, No. 66724" after mill crushing using a "Ball Mill Roller Crusher, Pascal Energy Company Ltd, No. 14429" in the Chemical Engineering Laboratory of the Rivers State University of Science and Technology, Nkpolu, Port Harcourt.

Porosity: A 200ml of activated carbon sample was weighed using an Analytical Weighing Balance, Denver Germany, model AE223, 03/2015   and poured into a 300ml cylindrical beaker. A measure of 100ml of distilled water using a measuring cylinder was poured into a calibrated cylinder. The water was then slowly poured into the beaker containing the activated carbon until the water got to the surface of the activated carbon which was obtained to be 270ml. The value was recorded and input into the mathematical expression below:

$$\% Porosity = \left(\frac{Volume\ of\ Water\ added}{Total\ Volume\ in\ AC} \right) \times 100$$

$$(5)$$

$$\% Porosity = \left(\frac{270}{300} \right) \times 100$$

$\% Porosity = 90\%$

Surface Area: The Brunauer Emmett Teller (BET) theory which is based on the concept that an adsorbed molecule is not free to move over the surface, and which exerts no lateral forces on adjacent molecules of the adsorbate. But that different numbers of adsorbed layers are allowed to build up on different parts of the surface.

$$\frac{P}{V(P^0 - P)} = \frac{1}{CV_m} + \frac{C-1}{CV_m} \cdot \frac{P}{P^0}$$

$C = e^{(q_1 - q_L)/RT}$ (C: constant)

Vm: Monolayer adsorption amount

V: Adsorption amount at the equilibrium pressure P

(Richardson et al, 2002)

P = saturated vapour presure

$$S_{BET} = \frac{Vm}{22414} \cdot 6.02 \times 10^{23} \cdot \sigma \cdot 10^{-18} \qquad (6)$$

N = (Avogadro's number) = 6.025×10^{23} molecules/mol
σ = (X-Sectional Area of N_2 Molecule) = 0.162 nm^2
(One molecule of nitrogen adsorbed on alumina or activated carbon occupies 0.162 nm^2)

Most adsorbents are highly porous materials, and adsorption takes place primarily on the walls of the

pores or at specific sites inside the particle. Because the pores are generally very small, the internal surface is in order of magnitude greater than the external area and is often 500 to 1,000 m²/g (McCabe et al, 2005).

The various sample extracts collected at the different 'run time' intervals were sent to the laboratory and subjected to further analysis using the Atomic Adsorption Spectrophotometer (AAS), Analyst 200

model made by Perkins Elmer to determine the various concentration of the heavy metal of interest (Fe, Pb, Cd, Cu) present in the aqueous sample extracts and the result tabulated below

3. RESULTS

Table 1: Effect Of Time On Adsorption Capacity Of Fe, Cu, Pb, Cd With 1o Cm Bed And 10g Weight Of Adsorbent

S/N	Time (min)	Iron conc (ppm)	Copper conc (ppm)	Lead conc (ppm)	Cadmium conc (ppm)	Length of Activated carbon bed (cm)	Weight of Activated Carbon used (g)
1	0	0.1400	0.0438	0.0038	0.0020	10	10
2	10	0.1100	0.0021	0.0038	0.0020	10	10
3	20	0.0800	0.0021	0.0038	0.0018	10	10
4	30	0.0700	0.0017	0.0038	0.0013	10	10
5	40	0.0600	0.0017	0.0038	0.0009	10	10
6	50	0,0600	0.0017	0.0038	0.0006	10	10
7	60	0.0600	0.0017	0.0038	0.0002	10	10
8	70	0.0600	0.0017	0.0038	0.0002	10	10

Table 1 shows that the adsorbent produced from the dry empty palm bunch could remove iron, copper and cadmium from industrial effluent, except lead.
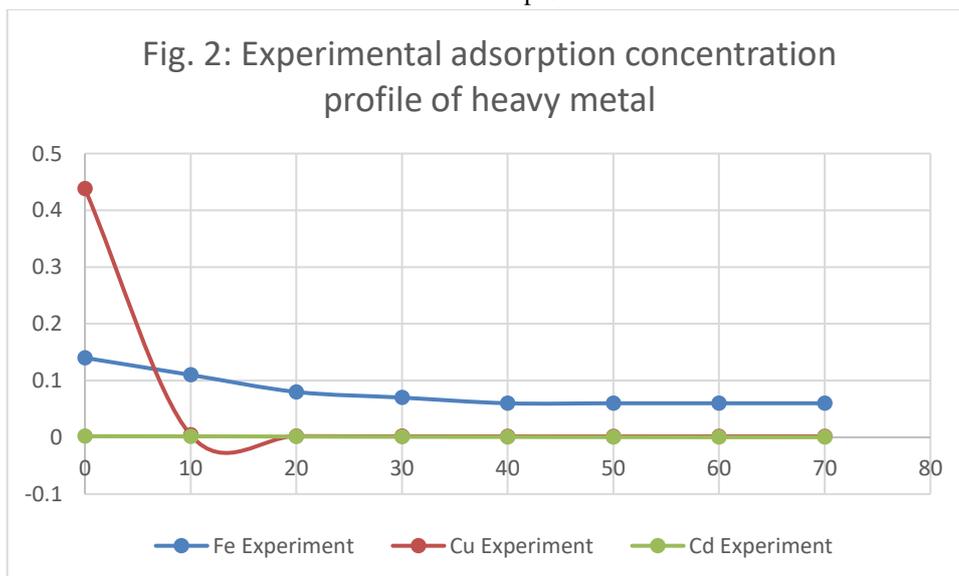
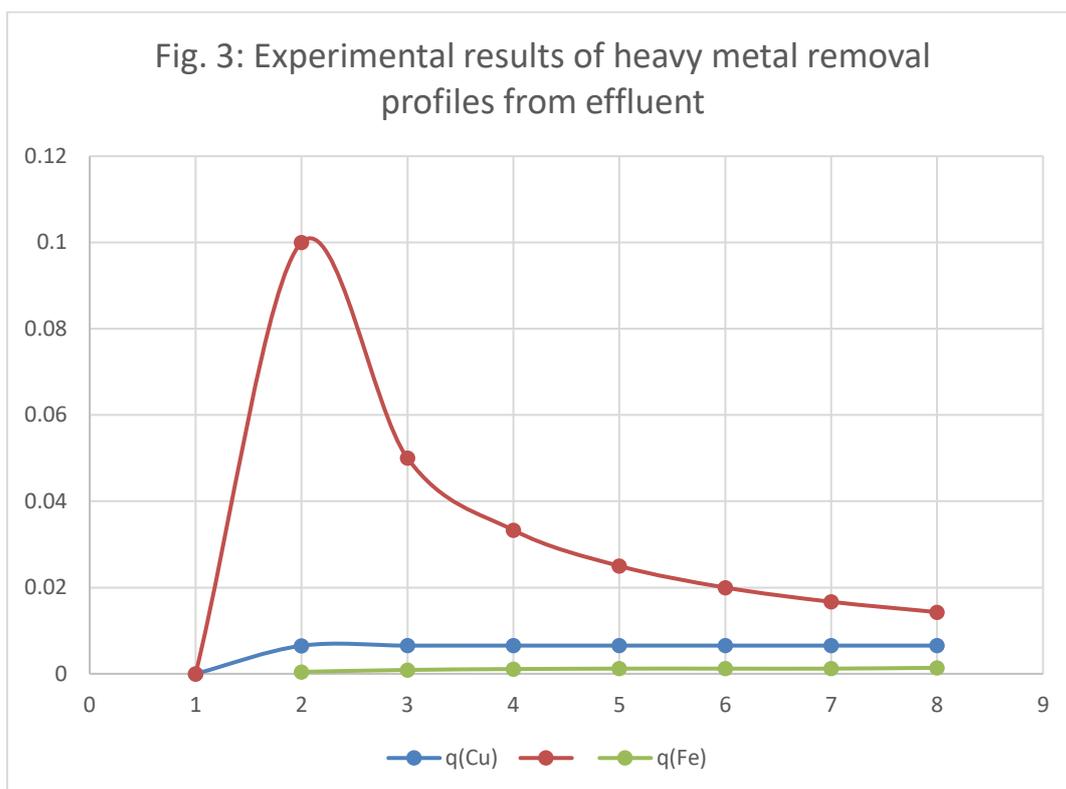**Table 2: Experiment and model results of heavy metals concentrations in liquid phase**

Time (min)	Fe Concentration (mg/L)		Cu Concentration (mg/L)		Cd Concentration (mg/L)	
	Experiment	Model	Experiment	Model	Experiment	Model
0	0.1400	0.1400	0.4380	0.4380	0.0020	0.0020
10	0.1100	0.1114	0.0042	0.2751	0.0018	0.0013
20	0.0800	0.0987	0.0021	0.2060	0.0013	0.0010
30	0.0700	0.0891	0.0019	0.1531	0.0009	0.0008
40	0.0600	0.0810	0.0017	0.1087	0.0006	0.0006
50	0.0600	0.0739	0.0017	0.0695	0.0004	0.0004
60	0.0600	0.0675	0.0017	0.0341	0.0002	0.0003
70	0.0600	0.0616	0.0017	0.0017	0.0002	0.0001

Fig 1: Model adsorption concentration profile results of heavy metals
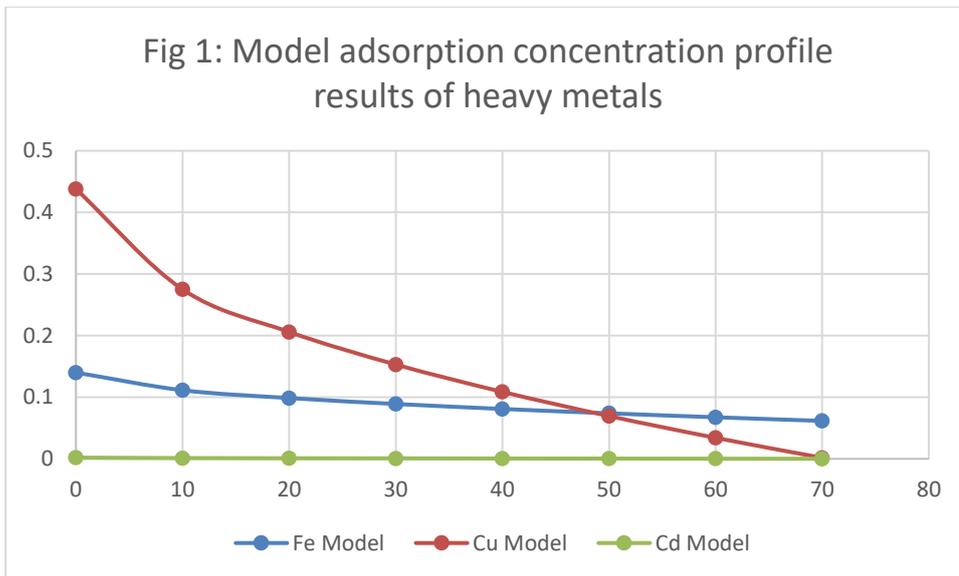
From the profile of the graph in figure 1 it will be observed that the adsorption of cadmium (Cd) onto the dry empty oil palm bunch sourced activated carbon modified with magnessium oxide remained unchanged initially and gradually progressing with time before attaining equilibruim at 60mins. From figure 2 it can be seen that the method is more effective in removing copper components from the wastewater stream as compared to iron and cadmiun. From profile, it was observed that the value of iron concentration in the model decreased at the same rate as that of experiemental value within the first 10 minutes. However, beyond which time the values of the iron concentration for the model were above those of the experiment but the different between the values of model and experiment was relatively insignificaant at the 70th minutes as can be seen in convergence in the profile.

Fig. 2: Experimental adsorption concentration profile of heavy metal

Fig. 3: Experimental results of heavy metal removal profiles from effluent

4. CONCLUSION

Based on the results of the experimental study of the techniques for removing heavy metal contaminants from industrial wastewater using activated carbon adsorbent locally produced from dry empty oil palm bunch modified with magnesium oxide, the following conclusions were drawn;

1. The locally produced activated carbon adsorbent was found to possess the characteristics and qualities of a commercial activated carbon when subjected to characteristics analysis.
2. The techniques of using the locally made activated carbon adsorbent modified with magnesium oxide was found to effectively remove iron, copper and cadmium traces but had no effect on the lead contaminant present in the wastewater stream.
3. The type of modifier used was found to play an important role in the kind/type of heavy metal contaminant of interest to be removed present in the wastewater stream.
4. The results obtained from the experimental analysis was validated with the model so developed and was found to favorably predict the progress of the adsorption process with time. The

profiles as shown in figures 2, 3 and confirm this assertion.

5. Adsorption technique was found to conform to Pseudo Second Order Kinetics.

Acknowledgement

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