Study on Phenol Adsorption by Activated Carbon Derived from Coconut Shell

Diptendu Datta[#], Sagar Biswas[#]

Department of Chemical Engineering, Heritage Institute of Technology, Kolkata-107

Abstract - **In the present study, adsorption of phenol from synthetic wastewater was investigated on metal impregnated activated carbon derived from coconut shell. Carbonized coconut shell mixed with appropriate metal salts was pyrolyzed at 850°C under inert N_2 atmosphere to develop metal impregnated activated carbon. In order to evaluate the performance of activated carbon thus prepared batch adsorption experiments were conducted at a fixed temperature (27°C) and pH (6.0) for different initial phenol concentration ranging from 100 to 500 mg.l^{-1}, with adsorbent loading of 0.2 gm in 200 ml adsorbate solution. The maximum adsorption capacity was found to be highest for 1% Zn-2% Fe-AC which was as high as 402 mg.g^{-1}. The adsorption isotherms were in conformation to both Langmuir and Freundlich isotherm model. Kinetic evaluation indicated that phenol adsorption on developed activated carbon followed pseudo-second-order rate reaction. Diffusion controlled kinetic model on the system showed that removal rate was controlled not only by intra-particle diffusion but also film diffusion.**

Keywords- Wastewater, Coconut Shell, Batch Adsorption, Activated Carbon, Metal Impregnation, Adsorption Isotherm, Kinetic Model.

I. INTRODUCTION

The rapid urbanization, unplanned industrialization and unskilled utilization of natural resources have led to the deterioration of ground water quality in significant part of the world particularly in developing countries. The deterioration of ground and surface water quality is a major cause of concern as they provide drinking water for more than half of nation's population, and is the only source of drinking water for many rural communities and some large cities. The presence of elevated concentration of phenol and its derivatives in river, lakes and sea water and other natural resources of water represents a major risk to plant, animal and human health [1]. Phenolic compounds are very harmful to all living beings even at low concentration because of its carcinogenicity properties. The health effect due to repeated exposure to low level of phenol in water includes liver damage, diarrhea, mouth ulcers, dark urine and hemolytic anemia [2]. Phenol finds its way into surface water from industrial effluents such as petrochemicals, plastics, paint, pharmaceuticals, steel industries and agricultural runoff etc [3]. Phenol has been registered as priority pollutants by the US Environmental Protection Agency (USEPA) with a permissible limit of 0.1 mg L^{-1} in wastewater [4].

The methods used for removal for the treatment of wastewater for the removal of phenol includes electrochemical oxidation, chemical coagulation, solvent extraction, membrane separation and photo-catalytic degradation using TiO_2, enzymatic polymerization and adsorption etc [5-9]. Coconut palm (Cocos *nucifera*) is grown through out the tropical world. It sustains livelihood of millions of people in costal regions of tropic. It ranks the seventh most important vegetable oil crop in the world. From 1980 to 2002, total world coconut productivity was increased significantly from 35 to 50 million tones [10]. Therefore, huge amount of solid waste are generated annually, mostly in the form of fiber and shell. The waste is either left to be rotten or used as a solid fuel which causes environmental hazards by generating carbon dioxide in air. Hence, the conversion of coconut shell solid waste into activated carbon therefore, serves a double purpose by converting unwanted surplus agricultural waste to useful, valuable material and provides efficient adsorbent material for the removal of organic pollutants from wastewater.

The process of manufacturing activated carbons involves two steps: the carbonization of raw carbonaceous material in an inert atmosphere and activation of the carbonized product. Activation can be done either physically or chemically or combination of both, known as physiochemical method. Physiochemical activation of carbonaceous compound is most desirable as it can produce high quality activated carbon with large specific surface area. Physiochemical activation mainly happened at elevated temperature ranging from 650 to 900°C in presence of dehydrating agents like KOH, $ZnCl_2$ or H_3PO_4 and oxidizing effect like CO_2 or steam. Hu et. al. developed activated carbon from coconut and palm shell through a single step physiochemical method using $ZnCl_2$-CO_2 and KOH-CO_2 [11,12].

This paper aims to present a comparative study on the adsorption properties of metal impregnated activated carbon prepared from coconut shell through physiochemical activation. Single and mixed metal (manganese, zinc and iron) impregnations with varying proportions of metal were performed in order to activate the char prepared from coconut shell for comparing their removal efficiency of phenol as a model adsorbate. Apart from this, the investigation also reveals adsorption equilibrium and isotherms, kinetic modeling and adsorption capacity studies of the particular batch adsorption system in details.

II. MATERIALS AND METHODS

A. *Preparation of Activated Carbons*

The raw material, i.e. coconut shells (agricultural waste materials) was collected from local market of the city of Kolkata, India. The collected material was thoroughly washed with double distilled water to remove any extraneous component and then sun dried for few days. It is then crushed to particle size of 1-2 mm. The shell was then carbonized at 850°C under the influence of nitrogen with a volumetric flow rate 150 cm^3 min^{-1} for 1h. For single metal impregnation of the char from coconut shell with manganese, zinc and iron, solution of $MnSO_4.H_2O$, $ZnSO_4.7H_2O$ and $FeSO_4.7H_2O$ respectively, were used. For 300 gm of clean and dry char, required amount of the appropriate salts were weighed out and dissolved in minimum volume of double distilled water (60-70 ml) and the solution was sprayed with mixing on the char. The mixture was then dehydrated on a drying oven at 110°C for overnight. Then 100 gm of dried solid mixture was taken in a cylindrical stainless steel reactor (6 cm inside diameter and length 20 cm) fitted with inlet and outlet tubes. The solid mixture was pyrolysed in the reactor under nitrogen atmosphere with a volumetric flow of 150 cm^3 min^{-1}. The pyrolysis was performed in a muffle furnace with controlled heating rate (1-3°C/min) upto 850°C. When the temperature of muffle furnace reaches at 850°C, it is kept constant for another 1h. The activated char was then cooled to room temperature under nitrogen influence and washed a few times with hot deionized water to unclog the pores from tar and other chemical residues. The washed activated carbon named according to the metal impregnation and its concentration and kept in air tight closed container.

A total of eleven different types of activated carbon were prepared with different combination of metals with their varying proportions. Nine types of activated carbons impregnated with single metal like manganese, zinc and iron each of three different concentration (1%, 2% and 3% by wt) and two types of mixed metal impregnated activated carbons (1% Mn-1% Zn-1% Fe and 1% Zn-2% Fe) were prepared according to the method described here.

B. *Characterization of Activated Carbon*

The activated carbon samples were characterized by determining their bulk density, pH of 1% suspension, iodine number, BET surface area and ash content. The chemical constituents of the activated carbon were determined following the methods given elsewhere [13,14]. The bulk density was measured by tapping method. The weighed amount (10 g) of dry activated carbon was taken in graduated glass tube and was gently tapped by a rubber pad until no further reduction of volume was noted. The weight/volume ratio provided the bulk density. Average of three measurements has been reported.

Surface area analysis of the activated carbon was carried out using Autosorb I.

For determination of pH of the prepared activated carbons, 1.0 g of each was stirred with deionized water (100 ml, pH 6.9) for two hrs and left for 30 h in an air tight stoppered conical flask. After the equilibrium time of 30 h, pH of the supernatant was measured using a digital pH meter.

Proximate analysis of the activated carbon was performed in order to determine fixed carbon, volatile matter, moisture and ash content. In inert atmosphere a small amount of sample was heated upto a temperature of 110°C for complete dehydration and followed by decomposition at 850°C to determine volatile matter and fixed carbon. The atmosphere was changed to oxidizing. The sample was exposed to 800°C in oxidizing atmosphere and maintained at this temperature until the weight remained unchanged.

Elemental analysis was performed using Elemental Analyzer (PerkinElmer 2400 Series II CHNS/O) to investigate the presence of elemental carbon, hydrogen and sulphur. The content of nitrogen and oxygen was determined from the difference of the total carbon, hydrogen and sulphur composition.

C. *Analysis of Phenol*

The concentration of phenol in the aqueous solution was determined using a UV spectrophotometer (Thermo Scientific Evolution 60S model) at a wavelength 270 nm [15].

D. *Sorption Procedure*

Adsorption studies were conducted in routine manner by batch technique [15]. The stock solution of phenol was prepared by diluting 1 g of the respective adsorbate with 1000 ml deionized water in an appropriate volumetric flask. The stock solution was then diluted to the desired initial concentration ranging from 100 to 500 mg l^{-1}. An amount of 0.2g adsorbent was added into 250 ml conical flasks filled with 200 ml adsorbate solution of known initial concentrations. All the sorption tests were conducted in slightly acidic (pH~ 6.0) aqueous suspension. The solution pH was adjusted by adding either a few drops of hydrochloric acid or sodium hydroxide (0.01M) as per requirement. The conical flasks filled with adsorbate solution and adsorbent were shaken in a shaker cum incubator kept at 27°C with shaking speed 125 rpm for 48 h. The samples were then withdrawn at appropriate time interval using a glass syringe to determine the residual concentration of adsorbate.

E. *Modelling: Equilibrium Isotherm Models*

The Langmuir and Freundlich models [16] were used to fit the adsorption isotherm and to evaluate the isotherm parameters. The linear form of Langmuir equation may be written in Eq. 1

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{a_L}{K_L}\right) C_e \qquad (1)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg g^{-1}), C_e the equilibrium concentration of solution (mg l^{-1}), K_L and a_L are Langmuir isotherm constants (l g^{-1}) and (l mg^{-1}), respectively. The model parameters can be obtained from the linear plots of C_e/q_e and C_e.

The linear form of Freundlich adsorption isotherm can be written in Eq.2

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \qquad (2)$$

where K_F the constant indicative of the relative adsorption capacity of the adsorbent (mg g^{-1}) and $1/n$ is the constant, indicative of the intensity of the adsorption known as heterogeneity factor. The model parameters can be obtained from the linear plots of $\log q_e$ and $\log C_e$.

F. *Kinetic Models*

To analyze the adsorption rate of phenols onto developed adsorbents pseudo-first-order and pseudo-second-order kinetic models were used. Lagergren based kinetic model and intra-particle diffusion model has been performed in this study in order to investigate chemical reaction as the rate controlling parameter for phenol adsorption mechanism. The pseudo-first-order equation may be written in Eq. (3).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (3)$$

where q_t is amount of solute adsorb per unit weight of adsorbent at time t (mg g^{-1}), k_1 is rate constant of pseudo-first-order sorption (h^{-1}). The adsorption rate parameter k_1 can be calculated by plotting $\log(q_e - q_t)$ and t.

The linear form of pseudo-second-order equation based on the equilibrium adsorption may be expressed in Eq. (4).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \qquad (4)$$

where k_2 is rate constant of pseudo-second-order sorption (g (h mg)$^{-1}$) and $k_2 q_e^2$ is the initial sorption rate. The values of k_2 and q_e can be calculated by plotting t/q_t and t.

The applicability of the model is verified through the sum square error (SSE) which is given by Eq. (5)

$$SSE = \sqrt{\frac{\sum\left(q_{t,\exp} - q_{t,calc}\right)^2}{N}} \qquad (5)$$

where N is the number of data points, $q_{t,\exp}$ is the amount of adsorbate adsorbed time t obtained from experiments (mg g^{-1}) and $q_{t,calc}$ is amount of adsorbate adsorbed at the same time t predicted from the models (mg g^{-1}).

III. RESULTS AND DISCUSSION

A. *Characterization of Adsorbent*

The yields of solid carbonaceous product derived from coconut shell were within the range of 27-33% (based on dry weight of charge, viz. metal impregnated activated carbon). The physical properties of the developed activated carbons are presented in Table I (all data presented in the table are the average of the 3 measurements).

The bulk density of metal impregnated activated carbons were found to be within the range of 0.42-0.51 gm cm^{-3} which is slightly lower range of commercial activated carbons. Low bulk density signifies greater void volume for adsorption. The higher adsorption capacity may also be verified from the iodine number and BET surface area measurement of the potential adsorbents.

Table I. Physical properties of metal impregnated activated carbon derived from coconut shell.

Type of Activated Carbons (AC)	Bulk Density (g cm^{-3})	pH of 1% suspension	Iodine No. (mg g^{-1})	BET surface area (m^2 g^{-1})	Leached metal conc. (ppm)
1% Mn AC	0.508	7.9	690	1010	BDL*
2% Mn AC	0.488	8.0	710	1005	BDL
3% Mn AC	0.484	8.0	725	995	0.06-0.07
1% Zn AC	0.496	8.2	780	965	BDL
2% Zn AC	0.479	8.3	830	960	BDL
3% Zn AC	0.480	8.5	860	955	BDL
1% Fe AC	0.471	8.6	790	995	BDL
2% Fe AC	0.475	8.7	810	990	BDL
3% Fe AC	0.492	8.7	825	985	0.1-0.12
1% Mn-1% Zn-1% Fe AC	0.434	8.7	980	950	0.03
1% Zn-2% Fe AC	0.425	8.7	1015	960	BDL

* BDL means <0.01 ppm

It is seen from Table I that with the increase of metal concentration potential adsorption site increases which is manifested form the enhanced value of iodine number and BET surface area. But the metal concentration cannot be increased indefinitely as it started to be leached from the aqueous suspension of adsorbent. Among the three heavy metals tested in this study, iron impregnation was found to be most effective to increase the degree of activation of carbon. Degree of activation can also be augmented by mixed metal impregnation without enhancing the threat of significant heavy metal leaching into the aqueous suspension. Zinc and iron impregnated activated carbon shows most satisfactory physical property with respect to iodine number that is very much comparable to commercial activated carbon.

The pH of the solution is one of the major factors influencing the adsorption capacity of the compounds that can be ionized. Acid or alkali species may change the surface chemistry of the adsorbent by reacting with surface groups. Since, 1% suspension of adsorbent shows alkaline nature, all the sorption test has been performed in a slightly acidic pH adding a very few drops of 0.01(M) HCl solution. Phenols being a weak acid will be adsorbed to a higher extent at lesser values of due to the attractive force prevailing at lesser pH [17].

Table II represents the proximate analysis of the activated carbons derived from coconut shells. The fixed carbon content was found to be very high with the range of 84-86%. This is due to pyrolytic effect at high temperature where most of the organic substances have been degraded into gaseous and liquid tar leaving a material with high carbon purity. Though virgin coconut shell derived activated carbons demonstrates low ash content (<0.6%) [15] but metal impregnated activated carbons yielded higher ash content probably due to the formation of metal oxide in oxidizing atmosphere. The elemental analysis of the produced activated carbon did not show any significance variation as the precursor remained unchanged.

Table II. Proximate Analysis of metal impregnated activated carbon derived from coconut shell.

Type of Activated Carbons (AC)	Proximate Analysis (%)			
	Moisture	Volatile Matter	Fixed Carbon	Ash Content
1% Mn AC	3.96	8.85	85.99	1.2
2% Mn AC	4.14	8.84	84.62	2.4
3% Mn AC	4.21	8.84	83.35	3.7
1% Zn AC	3.78	8.90	86.22	1.1
2% Zn AC	3.75	8.85	85.60	1.8
3% Zn AC	3.60	8.83	84.97	2.6
1% Fe AC	3.78	9.05	85.87	1.3
2% Fe AC	3.75	8.99	84.76	2.5
3% Fe AC	3.73	8.95	83.52	3.8
1% Mn-1% Zn-1% Fe AC	3.24	8.90	84.36	3.5
1% Zn-2% Fe AC	3.42	8.95	84.23	3.4

B. Effect of adsorption contact time

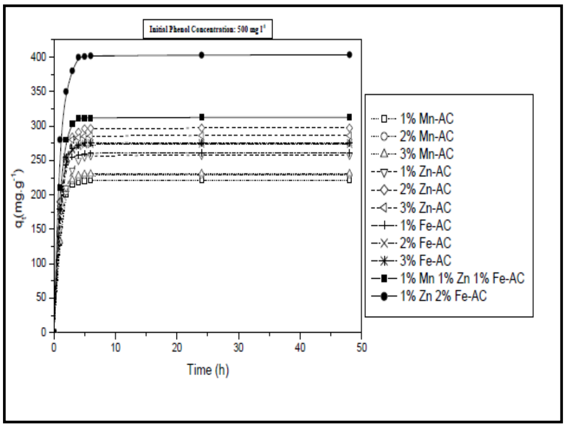

Fig. 1 Phenol adsorption profile on activated carbon derived from coconut shell (Initial concentration 500 mg.l^{-1}, 27°C, pH 6.0, adsorbent loading 1g.l^{-1}).

It was seen from the series of batch adsorption experiments that time to reach equilibrium is almost independent of initial phenol concentration and the type of adsorbent used. No significant rise of adsorbate concentration on the adsorbent was recorded after 6h of batch time. Fig. 1 illustrates the adsorption profiles of phenol on various adsorbents produced in this study at a fixed initial phenol concentration. The nature of all the adsorption profile are similar, closely resembles to the step response curve of first order system. Initially, a large number of vacant site are available for adsorption. Therefore, the adsorption rate is very fast and the adsorbate accumulated on the adsorbent surface mainly within the first 3h of the batch operation. As a result, the remaining vacant sites are difficult to be occupied due to the repulsive force between the phenol molecules on the solid surface and in the bulk phase [18]. Because of the small size of phenol, it can easily diffuse into the internal pores of the adsorbent resulting into reduction in driving force for mass transfer between the bulk liquid phase and the solid phase over time. Diffusion of phenol inside the pore also adds to the higher resistance for adsorption [19]. It is seen from Fig. 1 that the adsorption rate decreases drastically after 3h of operation for all adsorbents and reaches equilibrium after 5h.

C. Effect of initial concentration

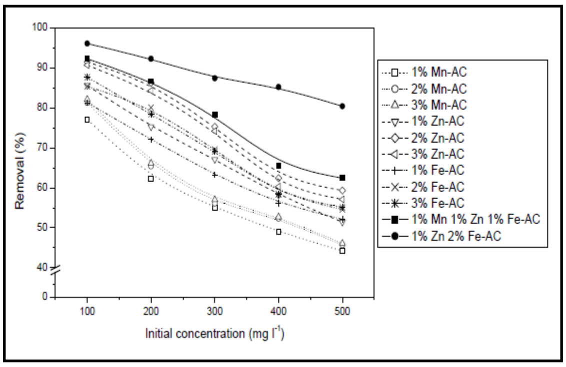

Fig. 2 Phenol removal profile by activated carbon from coconut shell with varying initial concentration of adsorbate (Initial concentration 100-500 mg.l^{-1}, 27°C, pH 6.0, adsorbent loading 1g.l^{-1}).

Fig. 2 illustrates the effect of phenol initial concentration on the removal percentage by the activated carbon developed in this study. The phenol removal percentage was found to decrease almost linearly with increase in initial concentration for all activated carbon samples. The effect of initial concentration on the percentage removal efficiency was minimum for mixed metal impregnated activated carbon. This implies higher uptake of phenol with increase in initial concentration of solution. But for single metal impregnated activated carbon the uptake of phenol did not increase to that extent which results into rapid fall of percentage removal efficiency with the increase of initial phenol concentration. Though the adsorption of phenol was higher than the reported phenol uptake trends by activated carbon without metal impregnation [20] but it cannot compete with the phenol adsorption capacity of mixed metal activated carbon. An increment of the uptake was due to greater driving force for mass transfer which impels more adsorbate to pass through from the bulk phase boundary to the solid adsorbent phase. It was also suggested elsewhere [21] that when the surface was almost saturated with adsorbate, the inter-particle diffusion will be activated and this will enhance the adsorption further but in a very slow manner as the adsorption takes place inside the carbon matrix.

D. Adsorption isotherm

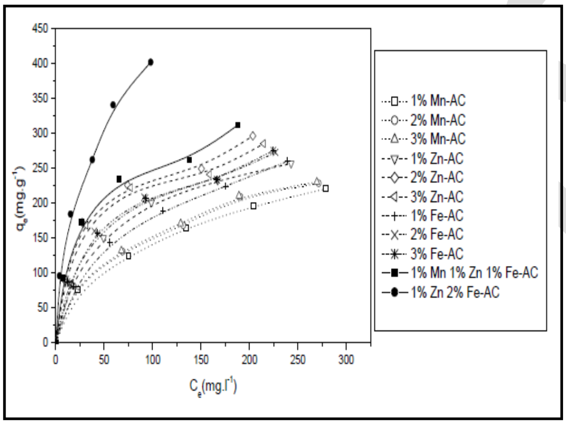

Fig. 3 Adsorption isotherm of phenol-activated carbon from coconut shell with varying metal concentration (Initial concentration 100-500 mg.l^{-1}, 27°C, pH 6.0, adsorbent loading 1g.l^{-1}).

Fig. 3 represents adsorption equilibrium curves at a constant temperature for different types of adsorbents prepared in this study. It was observed that with the variation of the types and metal percentage in the activated carbon equilibrium solute uptake onto the adsorbent changed significantly. The equilibrium adsorbate content (q_e) increases at a much faster rate with the increase in equilibrium solute concentration (C_e) for mixed metal impregnated activated carbons which is depicted by the farm line in Fig. 3.

The adsorption isotherm data were fitted with well known two parameters Langmuir and Freundlich isotherm models for better understanding of adsorption mechanism, surface properties and an affinity of the adsorbent.

Table III reveals the Langmuir and Freundlich isotherm parameter after linear curve fitting with appropriate co-ordinate system for phenol adsorption onto various adsorbent developed in this study. The regression coefficient values (R^2) shown in the table indicate that the phenol adsorption is well fitted to both Langmuir and Freundlich models with $R^2 > 0.9$ for all the cases analyzed. This signifies a possibility of mono and heterolayer phenol formation on the adsorbent surface. It may also be seen from Table III that for mixed metal impregnated activated carbon Freundlich isotherm model fits better than the Langmuir model which implies a heterolayer phenol formation on adsorbent surface.

Table III. Langmuir and Freundlich adsorption isotherm parameter

Type of Activated Carbons (AC)	**Langmuir Isotherm**			**Freundlich Isotherm**		
	K_L **(l.g^{-1})**	a_L **(l.mg^{-1})**	R^2	K_F **(mg.g^{-1})**	n	R^2
1% Mn AC	3.571	0.0107	0.998	20.17	2.347	0.973
2% Mn AC	4.91	0.0131	0.995	25.27	2.538	0.978
3% Mn AC	5.525	0.0135	0.991	26.39	2.577	0.985
1% Zn AC	6.849	0.0205	0.996	31.19	2.544	0.982
2% Zn AC	12.5	0.0275	0.985	48.18	2.907	0.954
3% Zn AC	11.49	0.0244	0.986	45.96	2.907	0.997
1% Fe AC	4.902	0.0147	0.994	22.47	2.227	0.984
2% Fe AC	7.976	0.0207	0.991	32.17	2.5	0.964
3% Fe AC	8.152	0.0195	0.986	35.06	2.617	0.985
1% Mn-1% Zn-1% Fe AC	13.15	0.0194	0.965	47.78	2.77	0.997
1% Zn-2% Fe AC	21.27	0.0305	0.961	52.96	2.237	0.998

The maximum monolayer adsorption capacity of adsorbent can be determined from Langmuir adsorption parameters. A bar chart representing monolayer adsorption capacity (K_L/a_L) according to Langmuir isotherm has been shown in Fig. 4 for various adsorbent based on the concentration of metal impregnation. It is observed that the adsorption capacity increases with metal impregnation concentration and also with mixed metal impregnation. The similar trend may also be observed from Freundlich adsorption parameter (K_F) shown in Table III for various adsorbents.

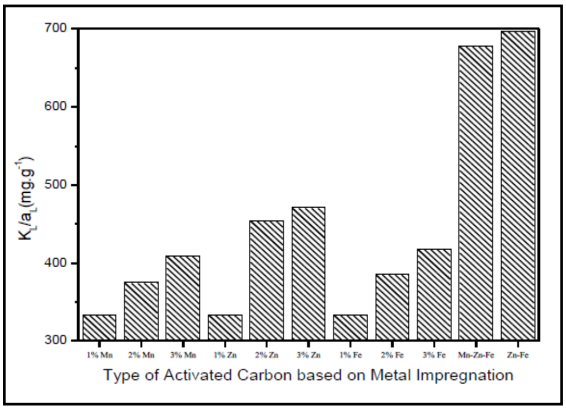

Fig. 4 Monolayer adsorption capacity (K_L/a_L) of phenol onto different types of activated carbon based on metal impregnation derived from coconut shell.

The essential characteristics of the Langmuir isotherm have been described in terms of a dimensionless constant separation factor or equilibrium parameter R [22], which is defined by Eq. 7

$$R = \frac{1}{1 + a_L C_0} \qquad (7)$$

where, a_L is Langmuir constant and C_0 is the initial concentration (mg.l^{-1}). R indicates the nature of adsorption as

$R > 1$ (unfavorable)
$0 < R < 1$ (favorable)
$R = 0$ (irreversible)
$R = 1$ (linear)

The value of R in the present investigation have been found to be below 1.0 for all adsorbent, indicating that the phenol adsorption onto metal impregnated coconut shell derived adsorbents is very favorable. The value of $1/n$ (where, n is freundlich adsorption parameter) are also found to be less than 1, which also verifies the favorability of phenol adsorption.

E. Adsorption kinetics

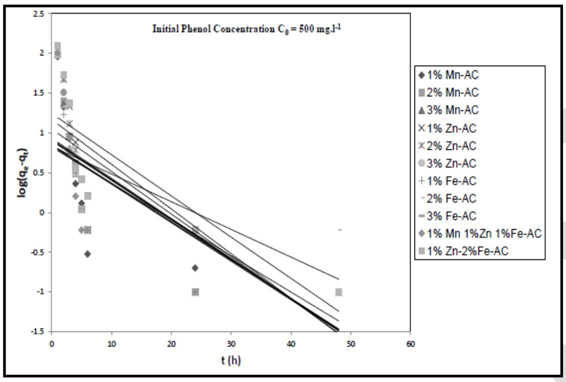

Fig. 5. Pseudo-first-order kinetic model plot for phenol adsorption onto different types of coconut shell derived activated carbon at fixed initial phenol concentration of 500 mg.l^{-1}.

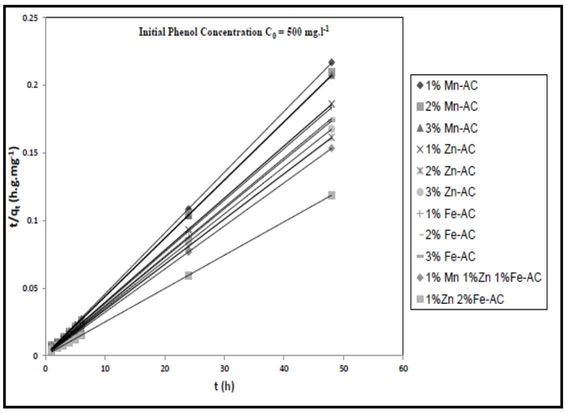

Fig. 6. Pseudo-first-order kinetic model plot for phenol adsorption onto different types of coconut shell derived activated carbon at fixed initial phenol concentration of 500 mg.l^{-1}.

The kinetic model studies were carried out at different initial phenol concentrations (100, 200, 300, 400, 500 mg.l^{-1}) for all types of adsorbent developed in this study. In order to analyze the effect of metal impregnation on kinetic model the calculated kinetic parameters have been shown in Table IV for a fixed initial phenol concentration of 500 mg.l^{-1}. Linear plots of pseudo-first-order and pseudo-second-order kinetic models have been shown in Figure. 5 and Figure. 6 respectively for the same initial phenol concentration.

Table IV. Comparison of pseudo-first-order kinetic model and pseudo-second-order kinetic model for phenol adsorption onto metal impregnated activated carbon (Initial phenol concentration, $C_0 = 500 mg.l^{-1}$)

Adsorbents	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	k_1(h^{-1})	$q_{e,cal}$ (mg.g^{-1})	SSE	k_2 (g.h^{-1}.mg^{-1})	$q_{e,cal}$ (mg.g^{-1})	SSE
1% Mn AC	0.1036	6.637	51.9	0.0222	222.21	1.59
2% Mn AC	0.1152	8.570	45.2	0.0192	230.43	0.97
3% Mn AC	0.1128	8.072	46.3	0.0195	232.56	0.84
1% Zn AC	0.1290	14.723	41.1	0.0128	259.74	1.06
2% Zn AC	0.1221	11.194	45.1	0.0151	298.51	0.79
3% Zn AC	0.1128	7.943	47.4	0.0208	287.35	0.43
1% Fe AC	0.1105	7.179	46.3	0.0234	262.47	0.92
2% Fe AC	0.0783	6.766	72.1	0.0225	273.97	0.63
3% Fe AC	0.1152	8.279	44.7	0.0217	277.00	0.36
1% Mn-1% Zn-1% Fe AC	0.1105	13.918	53.8	0.0203	313.48	0.31
1% Zn-2% Fe AC	0.1174	17.619	33.4	0.0129	404.86	0.27

It was seen that experimental data have no agreement with pseudo-first-order kinetic model for all initial phenol concentration tested in the present study due to the bigger error margin reported with the values of SSE. This may be verified from Figure. 5 and Table IV for initial phenol concentration of 500 mg.l^{-1}. However, phenol adsorption on activated carbon was found to be in conformation to pseudo-second-order kinetic model for all initial phenol concentration which suggests that chemical reaction is the rate controlling parameter. The model applicability is verified from Figure. 6 and also from calculated SSE values shown in Table IV which are less than 1.6. Therefore, it may be established that metal impregnation for activation of adsorbent can not alter the mechanism for adsorption. Though the mechanism remains unchanged, the rate constant k_2 varies with the metal concentration in the activated carbon. The rate constant k_2 was found to be decreased with increasing metal concentration excepting for zinc impregnation which implies that zinc impregnation enhances the overall rate of adsorption.

The initial phenol adsorption rates h (mg.g^{-1}.h^{-1}) can be calculated from the pseudo-second-order kinetic model by the Eq. 8

$$h = k_2 q_{e,cal}^2 \qquad (8)$$

and the result are plotted in Fig.7. It was found that the rate of adsorption increased with increasing concentration of metal in activated carbon with an exception of Manganese impregnation. This implies increasing metal concentration enhances degree of activation which ultimately results into higher driving force for mass transfer though the bulk concentration of phenol remain unchanged. The initial rate was most sensitive to zinc metal concentration in activated carbon as it increased more rapidly than the other metal studied. Mixed metal impregnated activated carbon yields highest initial rate as it gives most efficient activation to the carbon char.

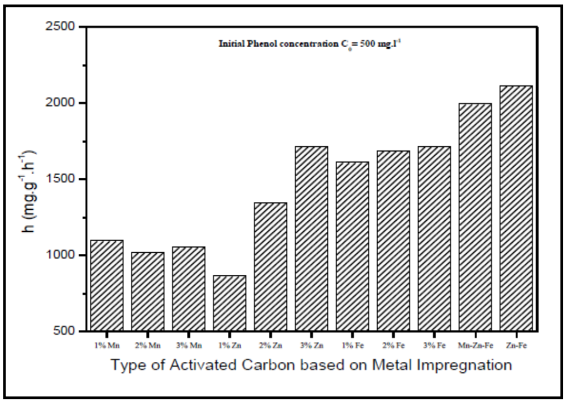

Fig. 7 The variation of initial rate of adsorption, h (mg.g^{-1}.h^{-1}) of phenol onto onto different types of coconut shell derived activated carbon at fixed initial phenol concentration of 500 mg.l^{-1}.

In order to gain insight into the mechanism and rate controlling steps affecting the kinetics of adsorption the kinetic experimental results were fitted to the weber's intra-particle diffusion model [23]. The intra-particle diffusion equation is expressed by Eq. 9

$$q_t = k_{id} t^{1/2} + c \qquad (9)$$

where, k_{id} is the intra-particle diffusion rate constant and intercept c represents the effect of boundary layer. The larger the intercept greater is the contribution of the surface sorption in the rate limiting steps. If the q_t versus $t^{0.5}$ is linear and the regression line passes through the origin, then intra-particle diffusion is the sole rate limiting steps.

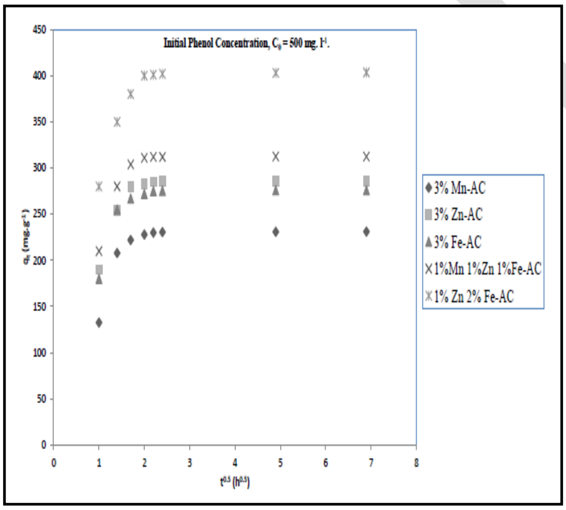

Figure. 8. Intra-particle diffusion model plot for phenol adsorption onto different types of coconut shell derived activated carbon at fixed initial phenol concentration of 500 mg.l^{-1}.

Since the variation of q_t with time was found to be similar at all initial phenol concentration and for all types of adsorbent studied here, Figure. 8, therefore, illustrate the representative plot of q_t versus $t^{0.5}$ at phenol concentration 500 mg.l^{-1} for the various metal impregnated activated carbon at highest concentration. The plots are not linear over the entire time range indicating more than one step affecting the phenol adsorption. Close observation indicates that adsorption mechanism of phenol on activated carbon for all conditions follow two linear parts. The first part attributed to film diffusion that start with rapid transport of adsorbate molecule on the external surface of the activated carbon through concentration boundary layer. The second part describes the gradual adsorption limited by the diffusion of solute in the liquid contained in the pores of adsorbent particle along the pore walls. It therefore, means that pores show resistance against the diffusion of phenolate ion into the inner adsorption site. It was also found from the regression analysis q_t versus $t^{0.5}$ data that intercept c are positive indicating phenol adsorption is controlled initially by film diffusion and then intra-particle diffusion. It was also observed that metal impregnation affected the c values showing an increasing trend with increasing metal concentration in the activated carbon. For mixed-metal impregnated activated carbon c values were found to be highest for all phenol concentration signifying the predominance of film diffusion over intra-particle mass transfer.

IV. CONCLUSION

In this study, activated carbon was prepared from coconut shell which is an agricultural waste found in plenty in tropical countries. The activation was carried out by manganese, zinc and iron metal impregnation with varying concentration and proportion. Though the BET surface area was found to be decreased with increasing metal concentration but degree of activation increased significantly augmenting the capacity of adsorption. Particularly for mixed metal impregnation the iodine number were comparable to commercial activated carbon.

All the eleven types of activated carbon prepared in the present study were found to be effective for the removal of phenol from aqueous solution. A conformation to most well-known adsorption isotherm models, Langmuir and Freundlich for all types of adsorbents indicates mono and hetero-layer phenol formation on the adsorbent surface. Single metal impregnation mainly promotes mono-layer adsorption but hetero-layer formation is more probable at higher concentration and mixed metal impregnation.

An agreement to pseudo-second-order kinetic model proves that chemical adsorption is the rate controlling process in this study. The mechanism of adsorption does not change with the degree of activation by metal impregnation. Film-diffusion followed by intra-particle pore diffusion controls the adsorption process. The generation of pores with large surface area provides ample space for the adsorption sites thus improving the phenol uptake.

Results of the study shows that metal impregnated activated carbon thus prepared can be used as potential adsorbent for phenol in wastewater. This findings, therefore, strengthens the credibility of agricultural solid waste particularly coconut shell as a potential activated carbon precursor.

ACKNOWLEDGEMENT

The authors acknowledge the funding provided by the Heritage Institute of Technology to carry out research work for graduate and post graduate students.

REFERENCES

[1] A. Bhatnagar, Removal of bromophenols from water using industrial wastes as low cost adsorbents, J. Hazard. Mater. 139 (2007) 93–102.

[2] ATSDR (Agency for Toxic Substances and Disease Registry), Toxicological Profile for Phenol, US Department of Health and Human Services, USA, 1998.

[3] V.K. Gupta, S. Sharma, I.S. Yadav, D. Mohan, Utilization of bagasse fly ash generated in the sugar industry for the removal and recovery of phenol and p-nitrophenol from wastewater, J. Chem. Technol. Biotechnol. 71 (1998) 180–186.

[4] USEPA, Technical Support Document for Water Quality Based Toxics Control. EPA/440/485032, United States Environmental Protection Agency, Washington, DC, USA 1985.

[5] K. Juttner, U. Galla, H. Schmieder, Electrochemical approaches to environmental problems in the process industry, Electrochim. Acta 45 (2000) 2575–2594.

[6] M. Tomaszewska, S. Mozia,W. Morawski, Removal of organic matter by coagulation enhanced with adsorption on PAC, Desalination 162 (2004) 79–87.

[7] A. Agrios, K. Gray, E. Weitz, Photocatalytic transformation of 2,4,5- trichlorophenol on TiO_2 under sub-band-gap illumination, Langmuir 19 (2003) 1402–1409.

[8] LD. Buchanan, J.A. Micell, Peroxidase catalyzed removal of aqueous phenol, Biotechnol. Bioeng. 54 (1997) 251-261.

[9] M.C. Burleigh, M.A. Markowitz, M.S. Spector, B.P. Gaber, Porous polysilsesquioxanes for the adsorption of phenols, Environ. Sci. Technol. 36 (2002) 2515-2518.

[10] J.E.G. van Dam., Coir processing technologies, Improvement of drying, softening, bleaching and dyeing coir fibre/yarn and printing coir floor coverings, Technical Paper No. 6, Wageningen, Netherlands, FAO and CFC 2002.

[11] Z. Hu, H. Guo, M.P. Srinivasan, N. Yaming, A simple method for developing mesoporosity in activated carbon, Sep. Purif. Technol. 31 (2003) 47–52.

[12] Z. Hu, M.P. Srinivasan, Mesoporous high-surface-area activated carbon from fir wood by KOH etching and CO_2 gasification for adsorption of dyes and phenols from water, J. Colloid Interface Sci. 294 (2006) 21-30.

[13] Al. Vogel, A Text Book of Quantitative Chemical Analysis, ELBS Publication, London, England, 1991.

[14] G. McKay, Use of Adsorbents for the Removal of Pollutants from Wastewater, CRC Press, Boca Raton, FL, 1995.

[15] A.T. Mohd Din, B.H. Hameed, A.L. Ahmed, Batch adsorption of phenol onto physiochemical-activated coconut shell, J. Hazard. Mater. 161 (2009) 1522-1529.

[16] W.J. Weber Jr., J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanit Eng. Div. ASCE 89 (1963) 31–59.

[17] N. Khalid, S. Ahmad, A. Toheed, J. Ahmad, Potential of rice husk for antimony removal, Appl. Radiat. Isotopes 52 (2000) 30–38.

[18] Mall L.D., Srivastava V.C. and Agarwal N.K. (2006). Removal of orange-G and methyl violet dyes by adsorption onto bagasse fly ash-kinetic study and equilibrium isotherm analyses, Dyes and Pigments, 69: 210-233.

[19] Srivastava V.C., Mall L.D. and Srivastava L.M. (2006). Equilibrium modellng of single and binary adsorption cadmium and nickel onto baggase fly ash, Chemical Engineering Journal, 117: 79-91.

[20] Allen S.J., Gan Q., Matthews R. and Johnson P.A. (2005). Kinetic modelling of the adsorption of basic dyes by kudzu, Journal of Colloid and Interface Science, 286: 101–109.

[21] Malik P.K. (2003). Use of activated carbons prepared from sawdusts and rice-husk for adsorption of acid dyes: a case study of acid yellow 36, Dyes and Pigments, 56: 239–249.

[22] Hall K.R., Eagleton L.C., Acrivos A. and Vermeulen T. (1966). Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions, Industrial and Engineering Chemistry fundamentals, 5: 212-223.

[23] Weber Jr. W.J. and Morris J,C. (1963). Kinetics of adsorption on carbon from solution, Journal of Sanitary Engineering Division, 89: 31–59.