Electrochemical Regeneration of a Native Activated Carbon

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Activated carbon prepared from coconut shell was examined for the adsorption of phenol from aqueous solution. The saturated activated carbon was regenerated using electrochemical method.

The native activated carbon was effective in adsorption of phenol. The uptake of phenol increased with increasing initial concentration of phenol. The equilibrium adsorption isotherm data was better fitted by the Langmuir model than the Freundlich model with regression coefficient of 0.99555 and 0.98409, respectively. The electrochemical regeneration efficiency was between 85 and 95 %, and an optimum condition of 50 mA regeneration current intensity and 5 h regeneration time at 1 % NaCl electrolyte solution was obtained.

Repeated regeneration of the activated carbon suggested continuous re-use of the carbon over a period of time.

Key words:
Activated carbon, electrochemical regeneration, adsorption

Introduction

Recent advances in carbon technology offer many potentials and unique challenges. For instance, a novel electrochemical separation process with carbon aerogel electrodes was developed recently, for removal of ionic impurities from aqueous streams, *Farmer*, [1995].[1] An innovative aerogel-based electrosorption process has been successfully used by *Tran* et. al. [1997][2] to remove heavy metals and inorganic salts from aqueous waste solution.

The production and processing techniques used in the manufacture of activated carbons depend on; nature and type of raw material available, desired physical form of the activated carbon, characteristics required for the intended application.[3] The activated carbon typically used in water treatment is coal, wood or coconut based. Peat and wood based raw materials are impregnated with a strong dehydrating agent; typically, phosphoric acid (H_3PO_4) or zinc chloride ($ZnCl_2$) mixed into a paste and then heated to temperatures of 500–800 °C to activate the carbon. The carbon formed generally exhibit a very `open' pore structure, ideal for the adsorption of large molecules.

Steam activation technique is generally used for the activation of coal and coconut shell raw material, which is usually processed in a carbonized form. Activation is carried out at temperatures of 800–1100 °C in the presence of steam.

It involves an endothermic Water-Gas reaction:

$$C + H_2O \rightarrow CO + H_2 - 175.440 \text{ kJ kmol}^{-1}$$

The temperature is maintained by partial burning of the CO and H_2 formed:

$$2\ CO + O_2 \rightarrow 2\ CO_2 + 393.790 \text{ kJ kmol}^{-1}$$

$$2\ H_2 + O_2 \rightarrow H_2O + 396.650 \text{ kJ kmol}^{-1}$$

Adsorption processes have been shown to be the most effective method for the removal of trace organic contaminant in water which is not biodegradable *Haghseresht* and *Lu*, [1998].[4] Adsorptive capabilities of activated carbon made it effective in this process.

Metcalf and *Eddy*, [1991][5] evaluated the various equations describing experimental adsorption isotherm data, and concluded that Freundlich and Langmuir isotherm described well the adsorption characteristic of activated carbons used in water and wastewater treatment, hence these two models were used in this study to analyze the adsorption equilibrium isotherm data.

The Freundlich isotherm,

$$\frac{\gamma}{\gamma_m} = k\gamma_f^{1/n}$$

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$\gamma = \gamma_0 - \gamma_f$ – initial mass concentration of solute (γ_0) minus the final mass concentration of solute (γ_f) in solution at equilibrium, mg L^{-1}, γ_m – mass concentration of adsorbent, g L^{-1}, k and n are empirical constants

The Langmuir equation on the other hand is

$$w_q = \frac{\zeta k_L \gamma_w}{1 + l_L \gamma_w}$$

where γ_w – aqueous phase equilibrium mass concentration, mg L^{-1}, w_q adsorbed phase eqilibrium mass, mg L^{-1}.

By rearrangement, it gives

$$\frac{\gamma_w}{w_q} = \frac{1}{k_L \zeta} + \frac{\gamma_w}{\zeta}$$

where k_L is Langmuir coefficient (L g^{-1}) and ζ is amount adsorbed per unit mass (g) adsorbent

Activated carbon, when used for the removal of organic compounds from gas or liquid phase systems, will gradually become saturated, due to the mass concentration of contaminants on the surface of the adsorbent. When this occurs a decision must be made on how to deal with the spent material. Usually, disposal of the spent material is considered the best option. However, activated carbon is a valuable commodity, which is capable of being recycled.

Several researchers had proposed several methods for regeneration of exhausted activated carbon. These include: desorption by an inert stream at low pressure, desorption at high temperature, desorption resulting from changing in affinity between adsorbate and adsorbent, desorption by extraction using strong solvents and removal of adsorbates by decomposition.[6–9] These methods are either thermal or chemical regeneration, especially, when carbon is saturated with organic pollutant such as phenol.[10] Thermal regeneration involves heat treating spent activated carbon in an inert atmosphere or air, whereas, chemical regeneration requires reacting exhausted activated carbon with appropriate chemical compound which desorbs the organic pollutant by chemical reaction. The thermal regeneration method though efficient is characterized by high loss of carbon to sintering and attrition,[11,12] also high energy requirement in maintaining the operation at such a high temperature required for the process, made the regeneration process expensive. As an alternative, *Zhang* and co-workers[13,14] proposed electrochemical regeneration technique. This is expected to favour in-situ regeneration of activated carbon especially for treatment of tap water and wastewater having phenol contamination.

Regeneration restores the activated carbon to a state where it is virtually identical in properties to the virgin pre-cursor. Undergoing the process of regeneration, rather than simply displacing adsorbed organic material by processing at high temperature, restores adsorptive capabilities of the active sites of the carbon. The organic compounds removed from the spent adsorbent are passed through a sophisticated multi-stage treatment system ensuring that regeneration system does not cause pollution while undertaking a recycling operation. Hence, electrochemical regeneration of the spent activated carbon is desired and formed the major thrust of this study. This project evaluates the effectiveness of the uptake of phenol by a native activated carbon from wastewater, electrochemically regenerates the activated carbon, and determines the efficiency of the regenerated activated carbon.

Materials and methods

Granular activated carbon used was made from coconut shell and supplied by Oyedele Group of Companies, Ojota Lagos. It was characterized at Federal Institute of Industrial Research Oshodi (FIIRO) Lagos, Nigeria, using the procedure of *Ahmedna* et. al. [1997].[15]

Electrochemical cell used was a laboratory scale cell model G0096, equipped with a rectifier (model G273), working electrodes and a Vycor membrane (Vycor number 7930), which separates the electrodes.

0.5 g-exhausted activated carbon was fixed on the electrodes using a porous cover and gases from the electrochemical reaction released easily. The activated carbon was used to adsorb phenol to saturation at room temperature; the saturated activated carbon was regenerated in the electrochemical cell reactor using 500 ml of 0.01 to 4 % electrolyte mass fraction. The saturation and regeneration process of activated carbon was repeated several times to determine the capacity of the activated carbon with the re-use.

The concentration of phenol in the solution was determined in a 721 type spectrophotometer using 4-amino-antipyrine fericyanide photometric method.

The regeneration efficiency η_{RE} of the native activated carbon was determined from the measured equilibrium adsorption values of phenol on fresh activated carbon (FAC_{sat}) and regenerated activated carbon (RAC_{sat}) as

$$\eta_{RE} = \frac{A_{RAC_{sat}}}{A_{FAC_{sat}}} \cdot 100$$

Results and discussion

The basic methodology used in obtaining the isotherm involved making a standard solution of phenol contaminant and diluting it to different standard mass concentration, mixing a fixed amount of adsorbent with the varying concentration of solution, and then allowing the mixture to equilibrate for 48 h. From the equilibrium solution, the amount of phenol adsorbed were determined and plotted against equilibrium concentration to give the isotherm.

The physical characteristics of the developed native activated carbon are reported in table 1. It has bulk density of 0.39 g cm^{-3} which is in the range of those reported in the literature[16]. It has a specific surface area of 1500 m^2 g^{-1} with a well developed porosity having a macrospore specific volume of 1.21 cm^3 g^{-1}. These characteristics favor high adsorption rates.

Table 1 – *Properties of the activated carbon*

Quantities	Value
bulk density	0.39 g cm^{-3}
particle density	0.59 g cm^{-3}
particle porosity	0.7 %
pore specific volume	1.21 cm^3 g^{-1}
specific surface area	1500 m^2 g^{-1}
mass fraction of ash	6.6 %
mass fraction of volatile sulphur	0.36 %
particle diameter	10 × 20 mesh

Figure 1 shows that adsorption of phenol onto the developed native activated carbon was favorable. The possible effect of various electrolyte on the adsorption equilibrium was evaluated by introducing 2 % of various electrolytes experimented into the solution. An enhanced adsorption isotherm (about 5 % rise) was noticeable. The Freundlich equation was fitted to the mathematical model of isotherm (Fig. 2). The constants k and n obtained were 7.2344 mg g^{-1} and 1.6160 by a line of best fit to the data on a linear regression analysis, respectively. The linear regression coefficient is 0.98409. Langmuir equation also gave ζ = 120.48 mg g^{-1} and k_L = 0.044 L mg^{-1} with linear regression coefficient of 0.99555 (Fig. 3). Between the two adsorption isotherm models used, the Langmuir model presented a better fit of the experimental data. How-

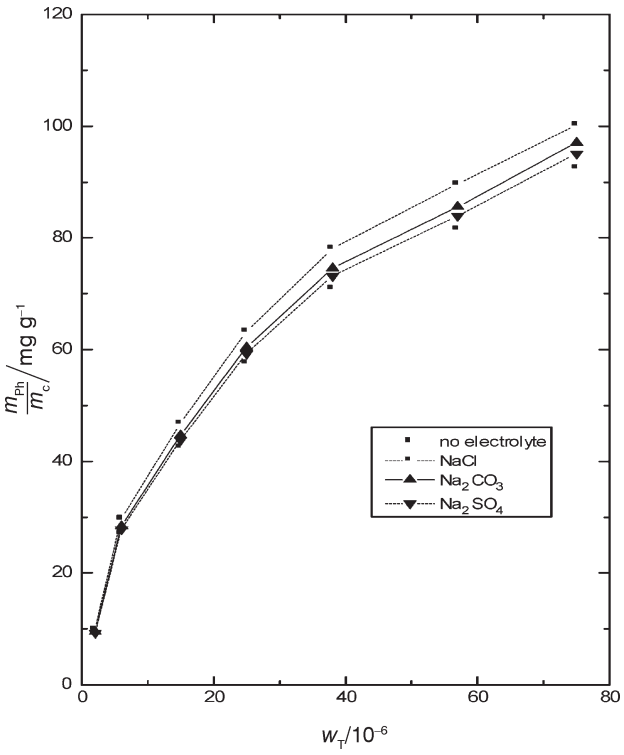


Fig. 1 – *Adsorption isotherm of phenol on native activated carbon*

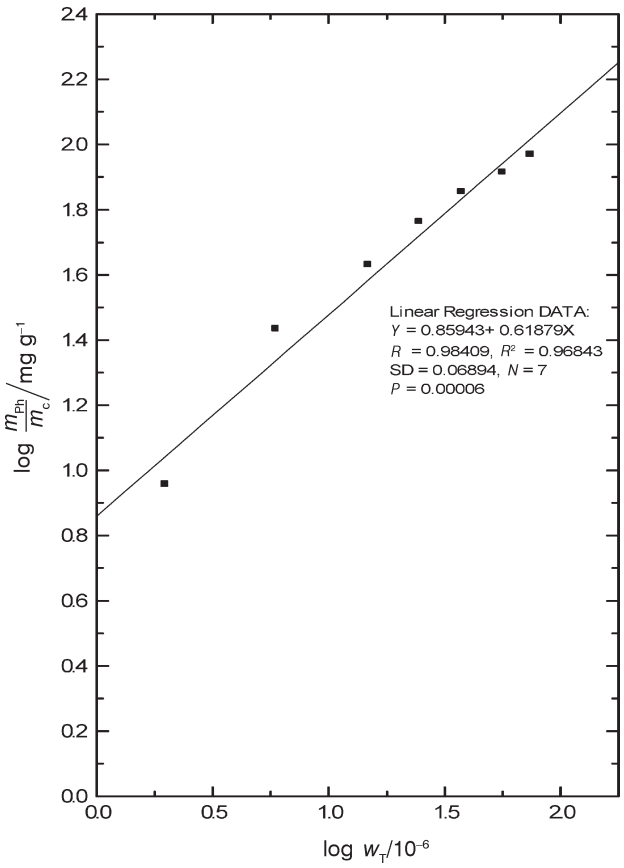
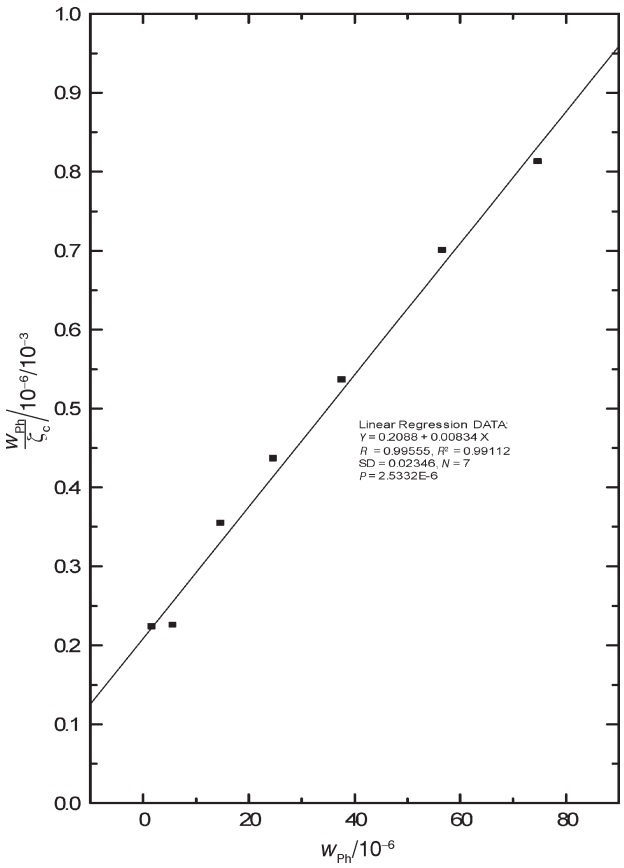
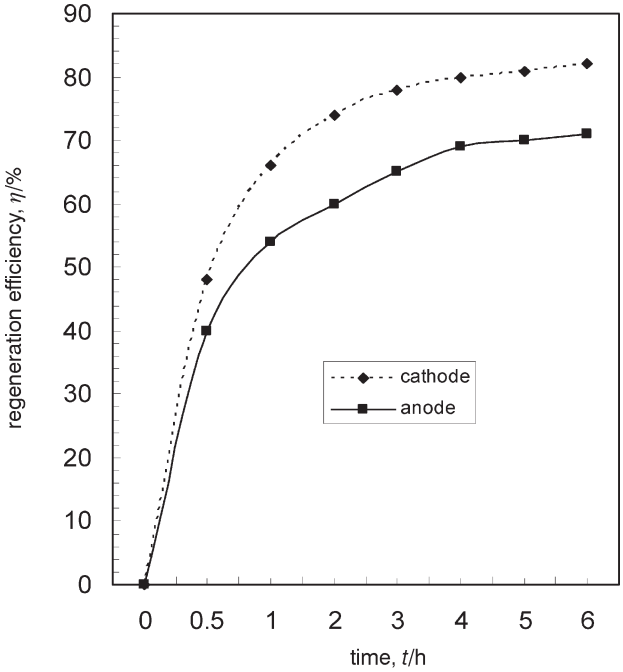


Fig. 2 – *Freundlich isotherm for the phenol adsorption on native activated carbon*



F i g . 3 – *Langmuir isotherm for the phenol adsorption on native activated carbon*



F i g . 4 – *Regeneration efficiency of activated carbon at 50 mA regeneration current intensity*

T a b l e 2 – *Variation of regeneration efficiency with electrolyte*

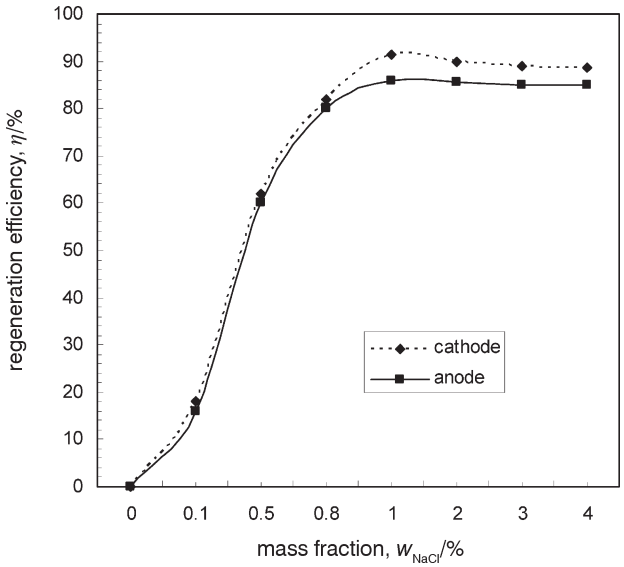
Electrolyte	Volume of electrolyte	Regeneration efficiency
	V / ml	η / %
NaCl	500	86
Na_2CO_3	500	70
Na_2SO_4	500	65

ever, the regression coefficient values showed that both models can adequately describe the adsorption process.

Regeneration of spent activated carbon was either at cathode or anode zones of the electrochemical cell. The experimental results showed that electrochemical regeneration is a good method with good regeneration co-efficient for the activated carbon. The influence of surface acidic functional group, applied potential and pH of the electrolyte on the adsorption capacity of the activated carbon, especially, application of cathodic external potential allow for electrochemical regeneration of the spent activated carbon. The process is a two-staged operation including firstly, desorption of phenol from the activated carbon, then oxidation by strong oxidant produced during the electrolysis.

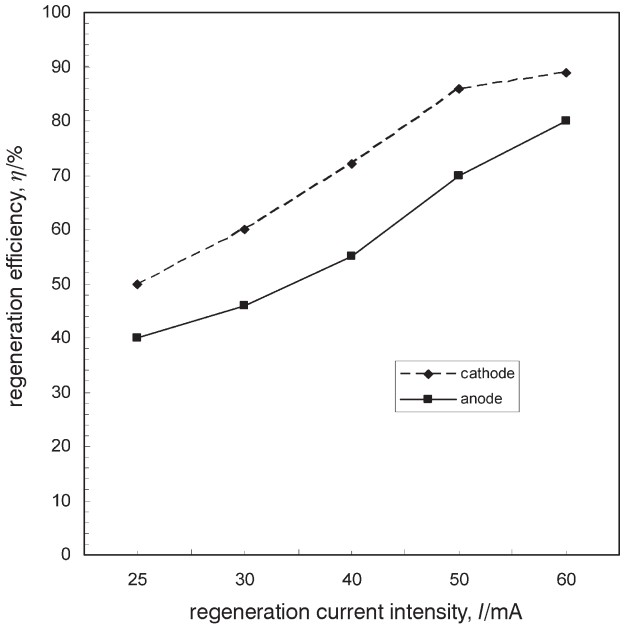
Figure 4 shows that the regeneration efficiency of activated carbon at the cathode is higher than at the anode. A general increase in regeneration efficiency with time irrespective of the electrode was also noticeable. This increase however became minimal after 5 h. Thus, a regeneration time of 5 h was used for subsequent determination.

From table 2, sodium chloride electrolyte solution, which gave the highest regeneration efficiency and low residual phenol, was most suitable for the electrochemical regeneration of the native activated carbon. The optimum NaCl concentration for the regeneration exercise was determined by increasing the electrolyte fraction from 0.1 % to 4 %. An initial increase in regeneration efficiency was observed up to 1 % and a gradual fall, although, not significant was obtained (Fig. 5). Hence, an optimum electrolyte mass fraction was assumed at 1 % and employed for subsequent characterization. A two staged regenerator process was easily noticeable as fog-like gas bubbles appeared at the electrodes and the electrolyte solution changed into dark brown colouration with offensive odour. This is the result of the release of phenol, followed by oxidation of phenol to yellow *p*-benzoic quinine, then to carbon dioxide and water. The response of regeneration efficiency to the change in regeneration current intensity was measured at 5 h regeneration time. An almost linear increase in regeneration efficiency of the coconut shell activated carbon



F i g . 5 – *Plot of regeneration efficiency at varying NaCl electrolyte mass fraction*

with increase in regeneration current intensity was obtained (Fig. 6). A regeneration current intensity of 45 to 50 mA is assumed ideal for the process, more so that a compromise has to be reached between the energy cost and time of processing to optimize profitability.



F i g . 6 – *Variation of regeneration efficiency with regeneration current intensity (Regeneration time: 5 h; 1 % NaCl electrolyte)*

Freundlich parameter k and Langmuir parameter ζ is a measure of adsorption capacity.[17] These parameters fell with repeated regeneration suggesting a decrease in adsorption capacity. This decrease however, becomes significant after the fifth regeneration cycle. The significant depletion might have resulted from the poisoning of active site of the activated carbon.

Conclusion

Granular activated carbon of coconut shell produced is highly effective in removal of phenol impurities from wastewater. Its regeneration using electrochemical method is very effective with regeneration efficiency greater than 85 %, using sodium chloride electrolyte. The regeneration efficiency increases with increasing regeneration current and electrolyte concentration. An optimum condition for the effective recovery of this native activated carbon's activity is 1 % NaCl electrolyte, 45–50 mA regeneration current intensity and 5 h regeneration time.

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