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Technical paper

Application of Freundlich and Temkin Isotherm to Study the Removal of Pb(II) Via Adsorption on Activated Carbon Equipped Polysulfone Membrane

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Abstract

The aim of this study was to investigate the application of membrane equipped activated carbon for heavy metal removal. An adsorption capacity of the activated carbon inside membrane matrix was performed against environmentally problematic ions specifically Pb^{2+}, in aqueous solution. The adsorption process was examined by Temkin and Freundlich isotherm. From the SEM observation, membrane exhibit sponge-like structure with dense micro-void formation across the matrix. This phenomenon was usually observed with membrane mixed with polyethyleneimine. For the adsorption studies, it is shown that Freundlich isotherm show better fit based on R^2 value of 0.9893 with Temkin isotherm fitted with R^2 of 0.9009. Through the fitted model, the adsorption occur on the surface of activated carbon are possibly multilayer type adsorption based on theory by Freundlich isotherm and fall under non-ideal reversible adsorption.

Keywords: *Activated carbon; Adsorption; Freundlich; Removal lead Pb(II); Temkin*

1. Introduction

Waste in general can be defined as discarded substances after completion of certain process. It is divided into several classification including domestic and industrial waste, schedule or chemical waste and municipal waste. All of these waste must be treated before released to environment. Heavy metal were usually part of the waste associated with plating industries leachate from landfill, groundwater contaminated by hazardous waste disposal site [1]. When the presence of heavy metal exceeding the acceptable limit, it has the potential to affect human physiology and disrupting other biological system. The irony of heavy metal waste is it could not be destroyed and will stay in the soil to affect human and living organism. One of the main contributor is increment of heavy metal demand in the industries especially in electronic and heavy metal are usually found in natural water resources [2]. All heavy metal is considered poisonous including lead where acute exposure might damage gastrointestinal tract and affect nervous system [3]. A prolong exposure to lead will probably cause learning disabilities among children, organ failure especially to kidney, liver and heart as well as immunity disorder [4].

Adsorption isotherm can be interpreted as curve mainly to explain the phenomenon involving retention of liquid or substances found in porous media or aqueous environment on a solid phase usually at constant condition of temperature and pH. This study focused on interaction of adsorbate with adsorbent when equilibrium established between metal ion on the adsorbent and surrounding metal ion in the solution [5]. In other words, adsorption equilibrium can be considered as an expression which show the correlation between the adsorbed amount and the remaining of adsorbent in the solution after being in contact for sufficient time where in the end a dynamic balance would be achieved corresponding to interface concentration and adsorbate concentration in bulk solution [6]. There exist several types of adsorption isotherm model including Langmuir, Freundlich, Temkin, Redlich-Peterson and et cetera.

Freundlich isotherm study the relationship which describes reversible adsorption limited to non-ideal and formation of multilayer. Unlike Langmuir isotherm that only focused on formation of monolayer adsorption. Freundlich isotherm explored the possibility to study a multilayer adsorption with heat and affinities scatter over a heterogeneous surface [7]. Freundlich isotherm are usually associated with heterogeneous system such as organic compounds, molecular sieves and interactive species found on activated carbon. However, there still limitation of choosing Freundlich isotherm because of lack fundamental thermodynamic basis when it is found not approaching Henry law at certain concentration.

This model demonstrates the ratio of the adsorbate onto a given mass of adsorbent to the solute was not a constant at different solution concentrations. The amount adsorbate is the total amount of the adsorption on all sites with the stronger binding sites must be occupied first until adsorption energy are exponentially decreased upon the completion of adsorption process. Nowadays, Freundlich isotherm is commonly applied in heterogeneous systems especially for organic compounds or highly interactive species on activated carbon and molecular sieves. However, at present, this type of isotherm is criticized for its limitation of lacking a fundamental thermodynamics basis, not approaching the Henry's law at vanishing concentration [6].

Temkin isotherm was developed to study the behaviour of hydrogen adsorption onto a platinum electrode inside acidic environment [6,8]. Several assumptions were proposed for the derivation of Temkin equation including the linearity of heat of sorption as a function of temperature rather than in logarithmic trends [8].

In recent years, membrane was conventionally used for filtration purposes. Although there exists system consist of membrane and activated carbon for adsorption process, the cost of maintenance is high and the overall system is expensive. Therefore, several idea or work has been proposed that could filter, disinfect bacteria and minimum space for installation. Still, the combination of various water treatment process would always give a clean and up to standard effluent quality [9]. This works will explore the possibility to incorporate activated carbon inside membrane matrix to provide heavy metal adsorption capability. Freundlich and Temkin isotherm were chosen to verified the adsorption process.

2. Materials and Methods

Both polysulfone pellets (PSU, average MW~35000) and polyethyleneimine solution (PEI, MW~25000; 50 wt% in H2O) and N-methyl-2-pyrolidone (NMP, 99.5%) were from Sigma-Aldrich (USA). Powdered activated carbon was used as adsorbent agent. Silver nitrate (98 % (AgNO3, Merck)) was used as antibacterial agent. Lead (II) nitrate was used to prepare synthetic waste water.

2.1. Adsorbent Preparation

First, N-methyl-2-pyrolidone (NMP), polyethyleneimine (PEI), silver nitrate ($AgNO_3$) and activated carbon (AC) were mixed until homogeneous. The composition is shown in Table 1. Next, polysulfone was added slowly into the solution to prevent agglomeration of polysulfone. The mixture was then stirred by using mechanical stirrer at low rotation per minute (rpm) and gradually increase at 100 rpm when polysulfone start to dissolved and stirring will continue until homogenous. In order to minimize vaporization of solvent, the prepared dope solution must be stored in tight glass container or bottle.

Table 1: Activated carbon filled membrane composition

Materials	Composition (wt%)
Polysulfone (PSU)	15
N-methyl-2-pyrolidone (NMP)	82.2
Activated Carbon (AC)	2.0
Polyethyleneimine (PEI)	0.3
Silver Nitrate (AgNO3)	0.5

Membrane was casted and fabricated by phase inversion method specifically by immersion precipitation technique where the dope solution was poured and layered onto glass plates followed by immersion into coagulant medium (water). Casted membrane was left for drying for 24 hours at room temperature (32^{o}C) before further characterization and testing.

2.2. Adsorbent Preparation

Membrane were characterized by Scanning Electron Microscopy (SEM) JEOL, Japan (Model JSM-6390LA) operated at 15kV for morphology analysis. For preparation, membrane was cut into rectangular strip before cryogenically fracture in liquid nitrogen to obtained clean break for cross section analysis. Then, coated with layer of gold under vacuum using Auto Fine Coater (JEOL JFC 1600, Japan). The cross section was observed under SEM at 2.0-2.5k magnification.

2.3. Adsorption Experiments

The adsorption process was conducted by stirring the sample at 250rpm with different concentration of heavy metal in synthetic waste water (10-100 mg/L). Then, the samples were left for 24 hours at room temperature (32^{o}C) to ensure all the solutions is in equilibrium. The water samples were sent for analysis using Atomic Absorption Spectroscopy (AAS) to quantified the amount of heavy metal left. Equilibrium data will be used to plot Freundlich and Temkin isotherm model. The linear and non-linear form of equations for both isotherm models are illustrate in Table 2.

Table 2: Equations for Langmuir and Freundlich isotherm models

Isotherm	Linear form
Freundlich	$\log q_e = \log K_F + \left(\frac{1}{n}\right)\log C_e$
Temkin	$q_e = \frac{RT}{b_T}\ln A_T + \left(\frac{RT}{b_T}\right)\ln C_e$

Where; q_e- amount of adsorbate adsorbed per unit weight of adsorbent (mg/g)
C_e-equilibrium concentration of metal ions in solution (mg/L)
b-energy of adsorption
n- adsorption intensity
K_F -Freundlich constant with multilayer adsorption which related to bond strength

The adsorption capacity was calculated using the equation below:

$$q_e = (C_i - C_e)V/m \tag{1}$$

Where q_e is the amount of metal ions adsorbed at equilibrium (mg/g), C_i is the initial concentration of metal ions in solution (mg/L), $C_e$is the equilibrium concentration of metal ions in solution (mg/L), V is the volume of heavy metal solution (L) and m is the mass of adsorbent (mg).

3. Results and Discussions

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3.1. Preparation of Membrane

Figure 1 show the cross-section image of pristine and activated carbon filled membrane. From the figure, a typical symmetric structure was developed for both membranes with sponge like pores. This phenomenon was caused by hydrophilic properties of polyethyleneimine that increase adsorption of water therefore excessive diffusion will occurs from intra molecular hydrogen bonding in non-solvent with functional group of membrane during phase inversion [10].

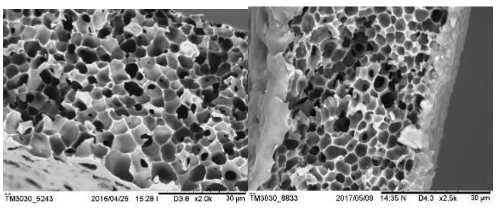
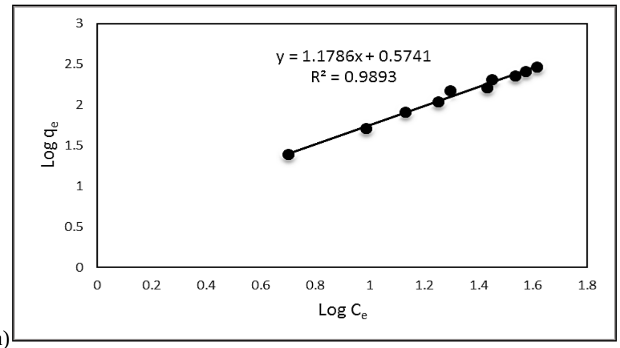


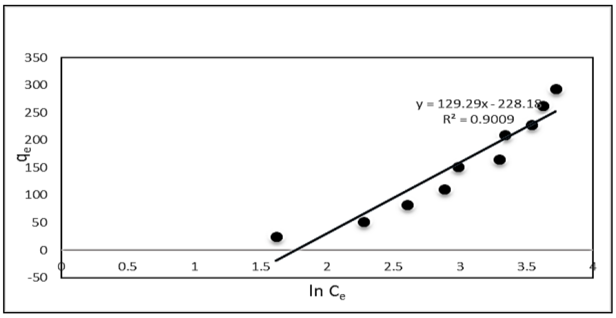
Fig. 1: SEM image for surface morphology for pure polysulfone membrane

3.2. Adsorption Experiment

The equilibrium data obtained for the adsorption of lead (II) were analysed by Langmuir and Freundlich as a widely method to study the relationship between equilibrium metal uptake (q_e) and final concentration at equilibrium (C_e). Figure 2(a) and 2(b) shows the plot for Freundlich and Temkin respectively.



(a)



(b)

Fig. 2: (a) Freudlich isotherm plot; (b) Temkin isotherm plot

Table 3 show the equilibrium data predicted using result obtained from the plot between log q_e and log C_e for Freundlich while plot between q_e and ln C_e for Temkin isotherm.

Table 3: Parameter of adsorption isotherm model

Isotherm	Parameter	Value
Freundlich	K_F	3.75
	n	0.84
	R^2	0.99
Temkin	A_T	0.47
	$B=\frac{RT}{b_T}$	297.70
	R^2	0.90

The linear equation of Freundlich isotherm is as follows:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{2}$$

where K_F is Freundlich constant and 1/n is an empirical parameter related to the adsorption intensity. The value of n determines the affinity of the process etiher chemisorptions ($n < 1$) or a physisorption ($n > 1$). From figure 2(a), Freundlich plot give 1/n value of 1.179 which indicate a physisorption has occurs. In general, physisorption are driven by van der Waals bond exist between adsorbate and adsorbent. Unlike chemisorption, physisorption postulated existent of multilayer adsorption on adsorbent which inline with Freundlich theorem. In addition, it is possible for value of n reaching 10 which show high adsorption intensity [11]. Although in this study the highest n are 0.8484 which fall under low adsorption intensity.

It was generally regarded that value of n in the range of 2 to 10 indicating high adsorption intensity, whereas less than 0.5 indicating low adsorption intensity. The result indicated high adsorption intensity of these ions with n of Cu^{2+}, Co^{2+} and Cr^{3+} were 7.457, 7.918 and 3.122, respectively.

Temkin isotherm is represented by the linear equation as follows:

$$q_e = \frac{RT}{b_T} lnA_T + \left(\frac{RT}{b_T}\right) lnC_e \tag{3}$$

Where A_T is the equilibrium binding constant corresponding to the maximum binding energy and constant $\frac{RT}{b_T}$ is indicates the heat of adsorption, where R is the universal gas constant, T is the absolute temperature in Kelvin and $\frac{1}{b_T}$ represents the adsorption potential of the adsorbent. All of these parameters were determined from the plot between q_e and lnC_e. In general, Temkin isotherm model was developed based on two assumptions where the heat of adsorption would decrease linearly and uniform distribution of binding energies up to some maximum binding energy [12].

Table 3 shows the calculated constants of the above isotherm equations. By comparing the R^2 values of these isotherms for the tested metal ions, we can find the most respective and suitable equation for fitting the experimental data. The nearest R^2 values to 1 belong to the Freundlich equation and this indicates that the respective equation fits with the experimental data best.

4. Conclusion

From the adsorption experiment, it can be concluded that, incorporation of activated carbon into membrane matrix show adsorption activities occurs and based on comparison of different isotherm models revealed that adsorption isotherm data were best fitted with Freundlich model which focussed on multilayer adsorption.

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