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“Adsorption of Phenol From Aqueous Solutions Using Incinerated Sewage Sludge”

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Abstract

A study had been carried out to determine the potential use of sewage sludge ash (SSA) as an adsorbent in removing phenol from aqueous solution. Batch kinetics and isotherm studies were implemented to evaluate the effect of initial phenol concentration and contact time of SSA. Results showed that the adsorption capacities of adsorbent (K_f) for phenol decreased from 14.89 mg/g to 0.68 mg/g as initial phenol concentration increased from 0.1 mg/l to 5.0 mg/l. Results revealed that solution with higher initial phenol concentration required longer time to reach equilibrium state. Adsorption capacity of adsorbent (K_f) decreased from 14.89 mg/g to 0.66 mg/g as contact time increased from 240 minutes to 1200 minutes. Adsorption isotherm analysis showed that the experimental data fit Freundlich model in most conditions.

Keywords: Adsorption; Phenol; Sewage Sludge Ash; Freundlich Isotherm

1. Introduction

Phenols are among the most common water pollutions and it is classified as an organic pollutant. Phenols are introduced into surface water from industrial effluents such as those from oil refineries and the coal tar, plastics, leather, paint, dyeing, pharmaceuticals and steels industries as well as from agricultural run off, domestic waste water and chemical spills (Singh and Rawat, 1994).

Phenol has been included in the USEPA list of priority pollutants (Azni and Katayon, 2003). Therefore the treatment of

them is a necessity. Several physical, chemical and biological processes are used for the removal of phenol from aqueous solutions. Chemical oxidation, liquid membrane, osmosis, chemical precipitation, filtration, electro dialysis and adsorption are among those methods most commonly employed (Azni and Katayon, 2003).

Adsorption is currently being used for the removal of organic and inorganic compounds from aqueous phases and since 1940s, activated carbon has become the water industry's standard for this purpose. Activated carbon is the most widely and effectively used adsorbent. A typical

activated carbon particle, whether in a powdered or granular form, has a porous structure consisting of a network of interconnected macropores, mesopores and micropores that provide a good capacity for the adsorption of organic molecules due to its high surface area. However this conventional activated carbon suffers from a number of disadvantages. It is quite expensive and the higher quality is desired the greater the cost would be. Therefore various attempts have been made by researchers to utilize another material to be converted as activated carbon.

In recent years, numerous low cost adsorbent materials have been evaluated for their capacity to remove phenol from aqueous solution. Among adsorbents that have been tested are bentonite (Banat *et al.*, 2000), rice husk (Munaf *et al.*, 1997), slash pine bark (Edgehill and Lu, 1998), fly ash generated in the sugar industry (Gupta *et al.*, 1998), fly ash from the thermal power station (Kumar *et al.*, 1987; Singh and Rawat, 1994) and local soil (Abuzaid *et al.*, 2000).

Sewage sludge is being generated in an ever increasing amount due to the rapid urbanization and higher effluent criteria implemented in recent decades. Without proper treatment and disposal, it will cause a secondary pollution problem in the environment. Generally, sewage sludge is carbonaceous in nature and rich in organic matter. Therefore, it has the potential to be used as activated carbon. This replacement could offer the combined benefits of reducing the volume of sludge and producing a valuable adsorbent with lower cost than commercial activated carbons

The objective of this paper is to evaluate the performance and effectiveness of incinerated sewage sludge in removing phenol by adsorption process. Adsorption isotherms were analyzed using the empirical Langmuir and Freundlich equation for its importance to describe how solutes interact with adsorbents in different initial phenol concentration and contact time.

2. Experimental

2.1 Preparation of adsorbent

The anaerobically digested and dewatered sewage sludge from sand drying bed was collected from Indah Water Konsortium Treatment Plant, Located in Damansara, Kuala Lumpur city, Malaysia. Dewatered sludge was introduced into an electrical oven (Mettler, model ULM400 Schwabach, Germany) at 105 °C for 24 hours and subsequently heated up to 900 °C inside muffle furnace (CWF 11/5, England) for a period of 3 hours to undergo drying and incineration process. After that, the sludge ash was then crushed using blender (National, model MJ-C85N, Japan) for a period of 30 seconds at medium speed. The incinerated sewage sludge was sieved using test sieve shaker (Endecotts Lombard Rd. London, model Sw193BR, England) with British Standard sieve BS410/1986 into a uniform size of 1.18 mm, 600 µm, 425 µm, 300 µm, 212 µm, 150 µm, 63 µm and 38 µm for a period of 15 minutes. The retained incinerated sewage sludge on each sieve was collected and kept inside desiccator. Particle sizes that were laid in the middle range (63 µm - 149 µm and 150 µm - 211 µm) were chosen for the study because the smallest size was dissolved and increased turbidity of water whereas the greater sizes was subjected to the less of surface area.

2.2 Analysis of phenol

Determination of phenol concentration was carried out according to Standard Methods for the Examination of Water and Wastewater (1999), using 4-aminoantipyrine method. The principle of this method is that phenols react with 4-aminoantipyrine at pH 7.9 ± 0.1 in the presence of potassium ferricyanide to form a colored antipyrine dye. This dye is extracted from aqueous solution with CHCl₃ and the absorbance is measured at

460 nm using spectrophotometer (HACH, DR-3000).

2.2 Adsorption kinetics experiments

Synthetic phenol solutions were prepared by weighting the purified phenol detached crystal (Fisher, UK) and dissolving them in distilled water. The adsorption kinetics of phenol solutions on sewage sludge ash was conducted at phenol concentrations (0.02, 0.1 and 5.0 mg/l) and a known weight of adsorbent dosage (0.5 - 7.0 g) which equilibrated for 0.25, 0.5, 1, 2, 3, 6, and 24 hours. A number of stoppered pyrex glass flasks containing a volume of phenol solutions with desired concentration ($C_o = 0.02, 0.1$ and 5.0 mg/l) and adsorbents (0.5 - 7.0 g) mixtures was placed on a flask shaker, SF1, UK (200 rpm) and was shaken at predetermined time intervals at original pH (9 - 12) and $T = 28 \pm 2$ °C. In order to study the effect of contact time on phenol removal study, the procedure was repeated with different contact time (0.25, 0.5, 1, 2, 3, 6, and 24 hours) at room temperature (28 ± 2 °C) where each one of this variable was set constant (initial phenol concentration, pH, particle size and adsorbent dosage). Initial phenol concentration was set to 0.02 mg/l, pH was set to original (9 - 12), particle size was set to 63 - 149 μm , and adsorbent dosage was set at 0.5 g. For each study effect, the solutions are sampled at desired interval times and filtered through glass microfibre filter paper, 47 mm ϕ (Whatman). Samples were kept for phenol analysis.

2.3 Adsorption isotherms

Adsorption is also a well known equilibrium separation process for wastewater treatment containing organics. Equilibrium studies on adsorption provide information about the capacity of the sorbent or the amount required to remove a unit mass of pollutant.

Generally, there are several models of adsorption isotherms have been published to describe experimental data of adsorption isotherms. The Langmuir and Freundlich models are the most frequently employed models. Both models are used to describe the relationship between the amount of phenol adsorbed and its equilibrium concentration in solutions at different parameters values. The Langmuir expression is represented by equation (1) :-

$$C_e / q_e = K_d / q_m + C_e / q_m \quad (1)$$

where q_m is the maximum adsorption capacity of adsorbents (mg/g), K_d is the equilibrium constant, C_e is the phenol concentration in solution at equilibrium (mg/l) and q_e is the amount of phenol adsorbed at equilibrium (mg/g).

The Freundlich equation has the general form and can be represented by equation (2) as :-

$$q_e = K_f C_e^{1/n} \quad (2)$$

$$\text{Log } q_e = \text{log } K_f + 1/n \text{ log } C_e \quad (3)$$

where K_f is the adsorption capacity (mg/g) and $1/n$ is the adsorption intensity.

q_e is calculated according to the following equation :-

$$q_e = V/M (C_o - C_e) \quad (4)$$

where V is the volume of the solution (l), M is the mass of the adsorbent (g) and C_o is the initial phenol concentration (mg/l).

The parameters in the models are estimated by fitting transformed data to be linearized forms of the models equation (1) and (3). The slope and intercept of the transformed data plots is used to estimate the two parameters in the Freundlich and Langmuir equations. For both isotherms, the constant is calculated from plots under different conditions (initial phenol concentration, and contact time).

3. Results and discussion

3.1 Phenol removal efficiency at different initial concentrations

The initial phenol concentration in aqueous solution is important since a given mass of adsorbent can only adsorb a fixed amount of phenol concentration. Hence, the more concentrated of solution it is, then the smaller volume of solution could be purified for a given mass of adsorbent. Fig. 1 shows the effect of different initial phenol concentration (0.02 mg/l, 0.1 mg/l and 5.0 mg/l) at a fix dosage of adsorbent of 7.0 g. It was observed that percentage of phenol removal decrease as initial phenol concentration increase.

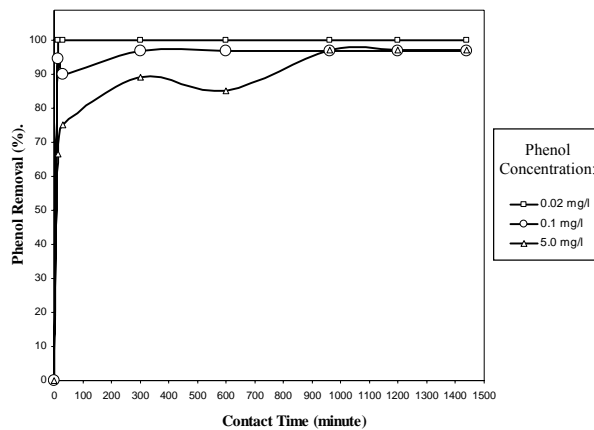


Fig. 1. Effect of initial phenol concentration on phenol removal efficiency (Adsorbent dosage = 7.0 g; pH = Original (9-12); Particle size = 63 - 149 μm)

As shown in Fig. 1, the removal of phenol reached to about 100 % for initial concentration of 0.02 mg/l. For 0.1 mg/l phenol solution, it was found that by adding 7.0 g of adsorbent the removal of phenol increased to 97 % in 300 minutes. For 5.0 mg/l phenol solution, the percentage of phenol removal also increased to 97 % with 7.0 g of adsorbent in 960 minutes.

3.2 Phenol removal efficiency at different contact time

Fig. 2 shows the effect of different contact time at a fix initial phenol concentration of 5.0 mg/l.

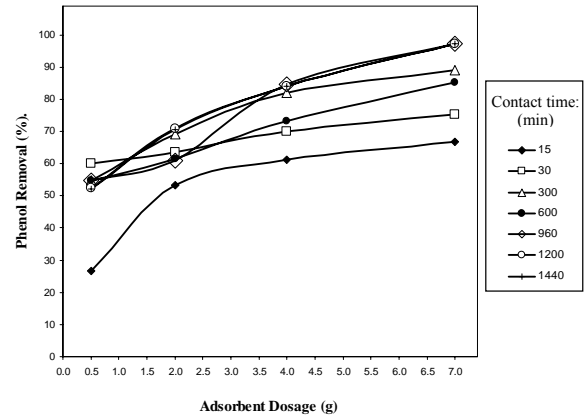


Fig. 2. Effect of contact time on phenol removal efficiency (Initial phenol concentration = 5.0 mg/l; pH = Original (9-12); Particle size = 63 - 149 μm)

As presented in Fig 2, for initial phenol concentration 5.0 mg/l, as the quantity of adsorbent increased from 0.5 g to 7.0 g, phenol removal increased from 27 % to 67 % for 15 minutes, 60 % to 75 % for 30 minutes, 55 % to 89 % for 300 minutes, 55 % to 85 % for 600 minutes, 55 % to 97 % for 960 minutes, 52 % to 97 % for 1200 minutes and 52 % to 97 % for 1440 minutes. When the solution was let to equilibrate at longer time (960 minutes) with the same amount of adsorbent added (7.0 g), higher phenol removal was achieved (97 %).

The result for the observed time was comparable with those reported for other adsorbents. Various equilibration times ranging from 2 hours (Azni and Katayon, 2003; Kumar *et al.*, 1987), 3 hours (Calace *et al.*, 2002; Rengaraj *et al.*, 2002) to 5 hours (Edgehill and Lu, 1998) have been reported for phenol. On the basis of these results, with the maximum of 7.0 g adsorbent dosage used, the sorption process can be considered very slow for 5.0 mg/l (16 hours).

3.3 Effect of initial phenol concentration on the adsorption isotherm parameters

The adsorption equilibrium data obtained for different range of initial phenol concentrations were applied to the Langmuir and Freundlich isotherms models and the isotherm constants from these plots were then calculated and are shown in Fig. 3 and Fig. 4.

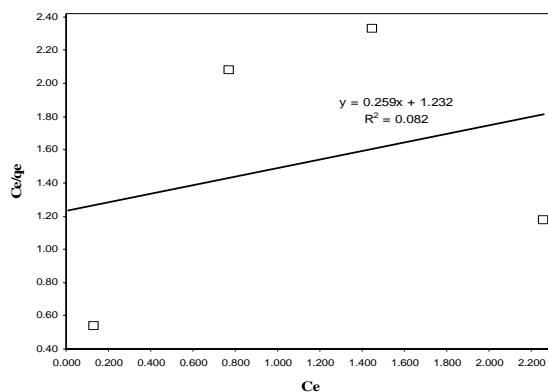


Fig. 3. Langmuir adsorption isotherm of sewage sludge for phenol at $C_0 = 5.0$ mg/l; $T = \text{Room}$ (28 ± 2 °C); $\text{pH} = \text{Original}$ (9 - 12), Particle size = 63 - 149 μm .

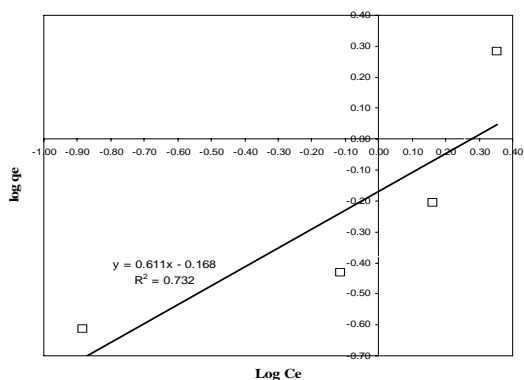


Fig. 4. Freundlich adsorption isotherm of sewage sludge for phenol at $C_0 = 5.0$ mg/l; $T = \text{Room}$ (28 ± 2 °C); $\text{pH} = \text{Original}$ (9 - 12), Particle size = 63 - 149 μm .

From Fig. 3 and Fig. 4, the isotherm data did not fit with linearized form of Langmuir for initial phenol concentrations

of 5.0 mg/l ($r^2 = 0.309$). However the isotherm data fit well with linearized form of Freundlich for phenol solution concentration of 5.0 mg/l ($r^2 = 0.732$).

Table 1. Sorption isotherm parameters for different initial phenol concentration (Particle Size = 63 μm - 149 μm ; $\text{pH} = \text{Original}$ (9-12)).

Initial Phenol Concentration C_0 (mg/l)	Langmuir			Freundlich		
	K_d	q_m (mg/g)	r^2	K_f (mg/g)	$1/n$	r^2
0.10	-0.03	-0.05	0.309	14.89	1.37	0.867
5.00	4.76	3.86	0.082	0.68	0.61	0.732

According to Table 1, the Freundlich adsorption capacity (K_f) for phenol was decreased from 14.89 to 0.68 mg/g as initial phenol concentration increased from 0.10 to 5.0 mg/l. Abburi (2003) reported that as initial phenol concentration increased from 1.0 to 11.0 mmoles/l, adsorption capacity of adsorbent (XAD-16 resin) for phenol (K_f) decreased from 0.4071 to 0.0748 mmol/g. Pan *et. al.*, (2003) also revealed the same situation where they found that adsorption capacity of adsorbent (polymeric) for phenol (K_f) was decreased from 7.77 to 5.31 mg/g as initial phenol concentration increased from 200 - 1400 mg/l. Compared to other researcher's results, adsorption capacity (K_f) for this study was considered higher when initial phenol concentration increased. Value of $1/n$ is found 1.37 (0.1mg/l) and 0.61 (5.0 mg/l). Abburi (2003) found value of n decreased (0.872) as initial phenol concentration increased (0.709). Pan *et. al.*, (2003) also discovered the same situation.

It has been reported the value of $1/n$ which laid between 0.1 and 0.5 show the best adsorption capacities (Asakawa and Ogino, 1984). However, Faust and Ally (1987) noted that value of $1/n$ that is closer to 1 indicates higher adsorptive capacity at higher concentration but rapidly diminishes at lower concentration. Therefore, this fact support the result of this study where adsorptive capacity is

greater at initial phenol concentration of 5.0 mg/l. The value of $1/n$ was found 0.61 which was closer to 1 compared to lower initial phenol concentration 0.1 mg/l where the value for $1/n$ exceeded 1. The increases of loading capacities of sorbent will increase phenol concentrations may also be due to higher interaction between substituted phenols and sorbents.

3.4 Effect of contact time on the adsorption isotherm parameters

The adsorption equilibrium data obtained for different range of contact time were applied to the Langmuir and Freundlich isotherms models and the isotherm constants from these plots were then calculated and are shown in Fig. 5 and Fig. 6.

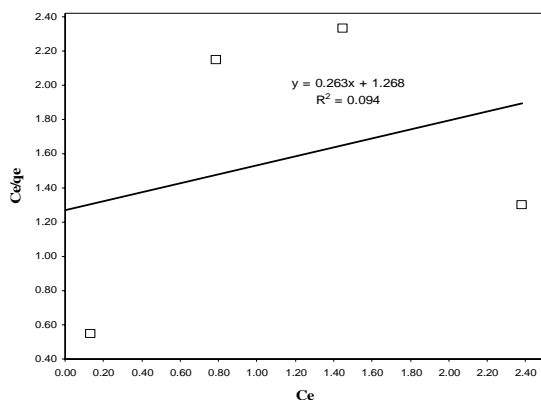


Fig. 5. Langmuir adsorption isotherm of sewage sludge for phenol at contact time = 1200 minutes (20 hours) for 5.0 mg/l; T = Room (28 ± 2 °C); pH = Original (9 - 12), Particle size = 63 - 149 μm .

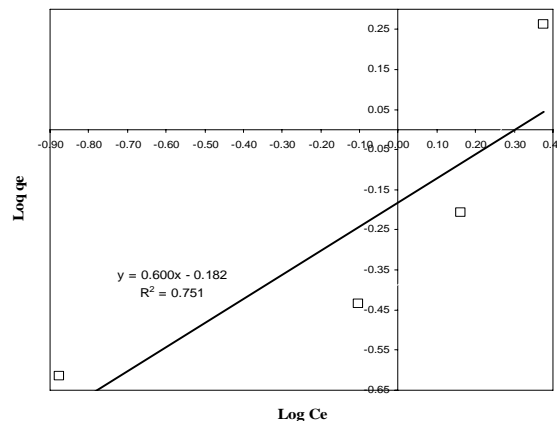


Fig. 6. Freundlich adsorption isotherm of sewage sludge for phenol at contact time = 1200 minutes (20 hours) for 5.0 mg/l; T = Room (28 ± 2 °C); pH = Original (9 - 12), Particle size = 63 - 149 μm .

According to the Fig. 5 and Fig. 6, the isotherm data did not fit with linearized form of Langmuir for 1200 minutes ($r^2 = 0.094$) contact times. However high values of $r^2 = 0.751$ revealed that the isotherm data fit well with linearized form of Freundlich 1200 minutes contact time.

Table 2. Sorption isotherm parameters for different contact time (Particle Size = 63 μm - 149 μm ; pH = Original (9-12).

Initial Phenol Concentration C_o (mg/l)	Langmuir			Freundlich		
	K_d	q_m (mg/g)	r^2	K_f (mg/g)	$1/n$	r^2
0.10 (240 minutes)	240	-0.03	-0.05	0.309	14.89	1.37
5.00 (1200 minutes)	120	4.83	3.81	0.094	0.66	0.60

As shown in Table 2, the Freundlich adsorption capacity of adsorbent for phenol, (K_f) was decreased from 14.89 to 0.66 mg/g as contact time increased from 240 minutes (0.1 mg/l) to 1200 minutes (5.0 mg/l). Tanaike *et. al.*, (2002) revealed that as contact time increased from 1 hour to 6 hours, adsorption capacity of adsorbent (air-oxidized carbon sphere) for phenol (K_f) was decreased from 43.6 to 16.2 mg/g. Wu *et.al.*, (2001) reported that as contact time increased from 5 to

90 minutes, adsorption capacity of adsorbent (montmorillonite) for phenol (K_f) was decreased from 2.244 to 5.936 mg/g. Therefore, adsorption capacity of adsorbent for phenol (K_f) for this study was smaller compared to above adsorbent when contact time increased.

Values of $1/n$ found 0.60 (5.0 mg/l) and 1.37 (0.1 mg/l). However, Tanaïke *et. al.*, (2002) found value of $1/n$ decreased from 0.23 to 0.36 as contact time increased from 1 hour to 6 hours. Wu *et.al.*, (2001) found same condition where value of $1/n$ decreased from 0.7545 to 0.3211 as contact time increased from 5 to 90 minutes. As discussed earlier, on the basis of these results, the adsorption capacities could be considered as good for higher concentration 5.0 mg/l however was less effective for 0.1 mg/l.

4. Conclusion

Sewage sludge ash (SSA) has been examined for potential utilization as low-cost material for the uptake of organic pollutant from wastewaters. The present study showed that the sewage sludge ash was an effective adsorbent for phenol removal from aqueous solution. Kinetic studies indicate that phenol removal decreased as initial phenol concentration increased for a given mass of adsorbent. The required contact time for phenol solution to reach equilibrium increased as initial phenol concentration increased for a given mass of adsorbent. For most phenols employed in this study, the adsorption capacities on SSA decreased as initial phenol concentration and contact time increased due to hydrogen-bonding interaction with the amino groups and the adsorbate molecules.

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