Adsorption of phenol from wastewater by peat, fly ash and bentonite

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Abstract

This study examined the effectiveness of less expensive adsorbents such as peat, fly ash and bentonite in removing phenol from wastewater by adsorption. Batch kinetic studies showed that an equilibrium time of 16, 5 and 16 h was needed for the adsorption of phenol on peat, fly ash and bentonite respectively. Batch studies indicated that the optimum pH for the adsorption of phenol on peat, fly ash and bentonite was between 4.0 to 5.0 at $21 \pm 1°C$. The adsorption of phenol on peat and bentonite was described well by the Freundlich isotherm whereas the Langmuir isotherm described the adsorption of phenol on fly ash. Peat, fly ash and bentonite were found to adsorb 46.1%, 41.6%, and 42.5% phenol respectively from an initial concentration of approximately 1 mg/l. © 1998 Elsevier Science B.V.

Keywords: Adsorption; Phenol; Peat; Fly ash; Bentonite

1. Introduction

Primary sources of phenolics are in wastewaters from benzene refining plants, oil refineries, coke plants, chemical operations, and plants which are processing phenols to plastics [1]. Phenols and related compounds are generally present in refinery and petrochemical wastewaters and are of particular significance as they are potentially toxic to humans and aquatic life, create an oxygen demand in receiving waters, and impart taste and odour to drinking water with even minute concentrations of their chlorinated

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Abbreviations: X, Amount of solute adsorbed, μg; M, Weight of adsorbent, g; C_e, Concentration of solute in solution at equilibrium, μg/l; K, Capacity coefficient; n, Intensity coefficient; a, b, Constants

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derivatives. Water treatment plants normally disinfect water by chlorination, consequently forming the undesirable chlorophenols when phenols are present.

Many researchers have shown that activated carbon is an effective adsorbent for organic compounds. specifically for phenolic compounds. However, its high initial cost and the need for a costly regeneration system make it less economically viable as an adsorbent. Cost effectiveness, availability and adsorptive properties, are the main criteria for choosing an adsorbent to remove organic compounds. Taking these criteria into consideration, many researchers have investigated the adsorptive properties of unconventional adsorbents such as polyurethane foam, olive shells, montmorillonite, peat, fly ash, red clay soil, and others.

The present study is undertaken with the following specific objectives:
1. to compare the performance and effectiveness of horticultural peat, fly ash and bentonite in removing phenol by adsorption from municipal wastewater;
2. to determine the effect of contact time and pH on the adsorption capacity of the above mentioned adsorbents;
3. to examine the desorption capacity of peat, fly ash and bentonite; and
4. to study the applicability of the Langmuir and Freundlich isotherms.

2. Materials and methods

The wastewater utilized in this study was raw wastewater collected from the City of Regina Municipal Wastewater Treatment Plant. The wastewater samples upon collection, were immediately acidified with concentrated sulphuric acid to a pH below 2.0 in order to avoid organic degradation by bacteria. Upon acidification, the samples were stored at 4°C before using them for the batch experiments. The characteristics of the raw wastewater is presented in Table 1. Since the city wastewater had only 15 to 39 $\mu g/l$ of

Table 1
Characteristics of wastewater

Characteristics	No. of samples	Range	Mean
pH	120	7.74–7.20	–
BOD	59	264–164.29	215.14
COD	25	615.29–446	527.29
DOC	23	35.43–23.57	29
SS	119	395.15–144.86	234.86
VSS	116	295.71–45.43	167.71
TKN	21	37.52–41.44	35.96
NH_3–N	21	20.16–24.08	22.81
PO_4–P	113	7.40–4.98	5.98
Phenol	3	39–15	24

All values are in mg/l except for pH and phenol concentration in $\mu g/l$.
BOD: biochemical oxygen demand; DOC: dissolved organic carbon; COD: chemical oxygen demand; SS: suspended solids; VSS: volatile suspended solids; TKN: total kjeldahl nitrogen.
Values of phenol concentration are based on the analysis conducted at the University of Regina; all the other values were obtained from the City of Regina Wastewater Treatment Plant.

Table 2
Typical analysis of sphagnum peat

Parameter	Value
Classification	Type 1: between Class A and B
pH	4.5–5.7
Salinity mmhos/cm	0.3–0.8
Moisture content, %	40–70
Bulk density, kg/m^3	62.3–118.7
Organic matter, %	90–95
Total nitrogen	0.8–1.0
Half saturation percentage	350–550
Nitrate, mg/l	118–397
Dilute acid soluble iron, %	80–250
Phosphorus, mg/l	80–250
Potassium, mg/l	650–2000
Calcium, mg/l	12 580–15 510
Magnesium,mg/l	4300–5550
Boron, mg/l	3–10
Manganese, mg/l	95–350
Total porosity, %	70–85
Screen size 9.51 mm, % retained	0–10
Screen size 6.35 mm, % retained	0–20
Screen size 2.38 mm, % retained	12–32
Screen size 0.50 mm, % retained	62–80
Surface area m^2/g	78.2
Cation exchange capacity meq/100 g	72.6

Source: Premier Peat, Carrot River, Saskatchewan.
Surface area and CEC value were determined at the University of Regina.

phenol, it was spiked to 1 mg/l to reflect the phenol content of certain industrial effluents such as paint manufacturing and hardboard manufacturing wastewaters which have phenol concentrations of 1.1 and approximately 1 mg/l respectively.

The sphagnum peat moss utilized in the study was horticultural peat manufactured by Premier Peat, Carrot River, Saskatchewan. Table 2 shows a typical analysis of peat. The peat moss passing through a number 20 sieve was dried at 103°C for 24 h before use.

The fly ash utilized in the study was collected from unit number 2 at the Poplar River Power Station operated by the Saskatchewan Power Corporation. Table 3 shows the composition of fly ash. The fly ash is produced as a result of the combustion of lignite coal and was obtained from the first bunker of the Poplar River's electrostatic precipitators. The fly ash was used as received and it did not receive any kind of pretreatment.

The bentonite used in the study was sodium bentonite mined by Canadian Clay Products, Wilcox, Saskatchewan. A typical analysis of bentonite is presented in Table 4. Table 5 shows the particle size and sub-sieve range data for bentonite. Similar to fly ash, bentonite was used in batch experiments without pretreatment.

2.1. Batch kinetic studies

Kinetics of adsorption of phenol by the adsorbents was studied in batch experiments by using an orbital shaker manufactured by Lab-Line Instruments, Melrose Park, IL,

Table 3
Typical analysis of fly ash

Constituent	Value	
SiO_2	50.70	
Al_2O_3	21.80	
CaO	11.50	
Fe_2O_3	4.50	
MgO	4.30	
K_2O	2.10	
TiO_2	0.80	
Na_2O	0.60	
SO_3	0.53	
BaO	0.20	
SrO	0.20	
P_2O_5	< 0.10	
Loss on ignition, %	0.84	
Copper, mg/l	67	
Nickel, mg/l	30	
Zinc,mg/l	57	
Chromium, mg/l	33	
Cadmium, mg/l	0.1	
Surface area, m^2/g	1.5–1.7	
325 mesh sieve, % retained	50–60	

The data were obtained from the Saskatchewan Power Corporation, Regina, Saskatchewan.
All values are in % weight/weight ignited unless mentioned otherwise.

Table 4
Typical analysis of bentonite

Constituent	Value	
SiO_2	61.4	
Al_2O_3	18.1	
Fe_2O_3	3.2	
TiO_2	0.1	
MgO	2.3	
CaO	0.6	
K_2O	0.4	
Na_2O	2.2	
H_2O (− 105°C)	9.0	
H_2O (+ 105°C)	5.0	
Trace Metals, mg / l		
Arsenic	< 10	
Copper	< 1.5	
Lead	< 10	
Mercury	< 2.5	
Cation exchange capacity meq/100 g	80–85	
Surface area, m^2/g	74.5	

Source: Canadian Clay Products, Regina, Saskatchewan.
All values are in % unless mentioned otherwise.

Table 5
Particle size and sub-sieve range data for bentonite

Particle size	% Retained on mesh
Screen size 150 microns	94.18
Screen size 200 microns	79.84
Screen size 75 microns	54.02
Sub-sieve range	*% Below*
20 microns	97.5
10 microns	93.8
05 microns	91.6
02 microns	91.3

Source: Canadian Clay Products, Regina, Saskatchewan.

USA. One hundred milliliters of the spiked wastewater containing about 1 mg/l of phenol was transferred to 250 ml pyrex glass beakers. In order to determine the equilibrium time for the adsorption of phenol on the adsorbent, a known weight of the adsorbent was added to each beaker containing 100 ml of spiked wastewater. Immediately the beakers were sealed with PARAFILM 'M' manufactured by American National CAN™, Greenwich, CT, USA. The beakers were covered to avoid vaporization losses of phenol from the wastewater. A control was set, to which no adsorbent was added to determine if phenol was adsorbed by walls of the beakers and the suspended solids present in the wastewater. To determine if phenol was being leached from the adsorbent during the study period, the same amount of adsorbent was added to 100 ml of deionized water and was shaken for the entire period along with the other samples. The prepared samples were shaken at 175 rpm at room temperature ($21 \pm 1°C$). The samples were covered during the entire experiment to avoid phenol degradation by photolysis.

The wastewater from each beaker was filtered and analyzed for phenol concentration after 0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, and 24 h in order to determine the equilibrium time required for the maximum adsorption of phenol onto the adsorbent. Equilibrium time was determined as the contact time required for the concentration of phenol in wastewater to reach an equilibrium. The wastewater containing the adsorbent was filtered through 0.45 μm glass fibre filter. The filtrate was distilled and phenol was extracted from the distillate by the chloroform extraction method [2], and the extract analyzed spectrophotometrically, using a Spectronic 21 spectrophotometer. All measurements were made at a wavelength of 460 nm corresponding to the maximum absorbance for phenol.

2.2. Batch adsorption studies

Experiments were conducted to determine the pH range at which the maximum adsorption of phenol would take place on the adsorbent. The wastewater was spiked to approximately 1 mg/l of phenol using the stock solution. The pH of the wastewater was then varied by the addition of 1 N H_2SO_4 or 1 N NaOH solution. Phosphate buffer was added to each sample to maintain the pH level. The pH was varied from 2.0 to 8.0.

After mixing for the established contact time, the final pH of the reaction mixture was recorded and the wastewater was filtered, distilled, extracted and analyzed for phenol.

Batch isotherm experiments were conducted for the adsorption of phenol on the adsorbent by adding to wastewater spiked to approximately 1 mg/l of phenol, with different amounts of adsorbent. The pH of the spiked wastewater was adjusted to an optimum pH obtained from the earlier study. The experiments were carried out at room temperature (21 ± 1°C). After the established contact time was reached, the wastewater was filtered, distilled, extracted and analyzed for phenol concentration.

2.3. Desorption studies

The desorption studies were carried out after the batch adsorption studies were conducted at room temperature. On completion of the batch adsorption study at room
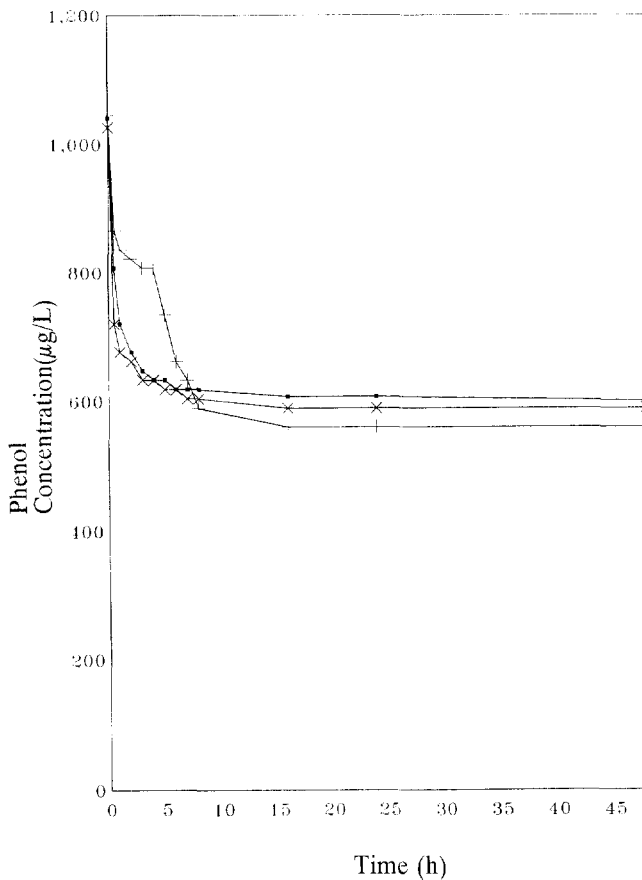

Fig. 1. Equilibrium time for the adsorption of phenol by peat, fly ash and bentonite at optimum pH (Peat ×, Fly Ash +, Bentonite ■).

temperature, the adsorbate was filtered out and added to 100 ml of deionized water; the beakers were sealed immediately with PARAFILM protected from light and shaken for 24 h at 175 rpm. After the study period, the contents were filtered, distilled, extracted and the extract analyzed for phenol concentration.

3. Results and discussion

Batch kinetic studies showed that an equilibrium time of 16, 5 and 16 h was needed for the adsorption of phenol on peat, fly ash and bentonite respectively (Fig. 1). Batch studies indicated that phenol was better adsorbed onto peat, fly ash and bentonite at pH values of 4.0, 5.0 and 4.0 respectively (Fig. 2).

pH
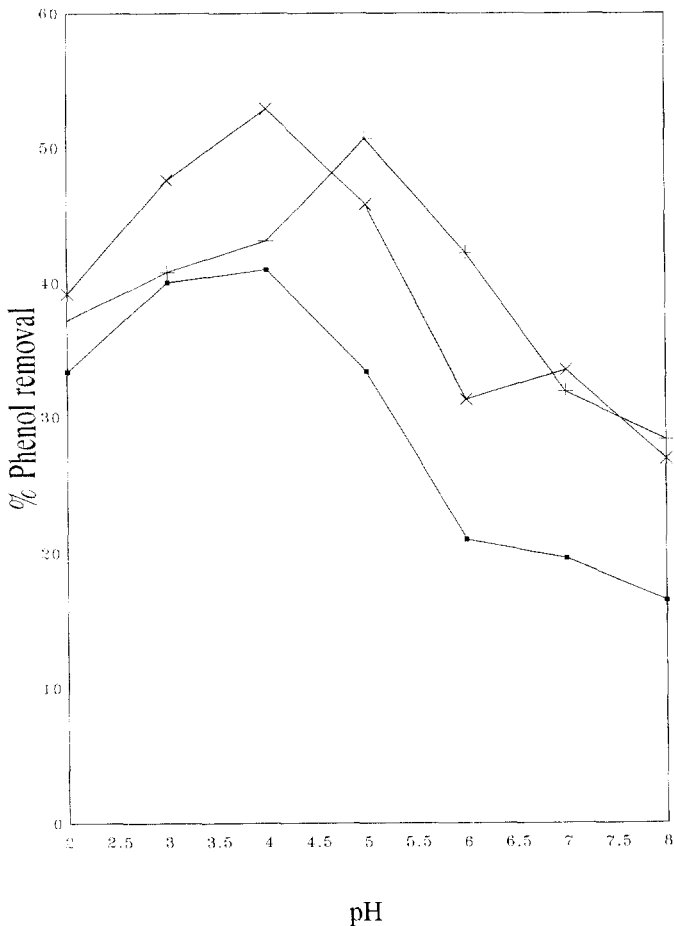
Fig. 2. Effect of pH on the adsorption of phenol by peat (×), fly ash (+), bentonite (■).

Table 6
Phenol adsorption on peat, bentonite and fly ash

Adsorbent	Model	Equation	Correlation Coefficient
Peat	Freundlich linear	$\log \dfrac{X}{M} = -3.34 + 1.89\log(C_e)$	0.86
	Freundlich non-linear	$\dfrac{X}{M} = 0.0362 \times C_e 1.57$	0.84
Bentonite	Fruendlich linear	$\log \dfrac{X}{M} = -10.29 + 3.99\log C_e$	0.86
	Freundlich non-linear	$\log \dfrac{X}{M} = 2.013 \times 10^{-1} 3C_e^{4.84}$	0.80
Fly ash	Langmuir linear	$\dfrac{C_e}{\left(\dfrac{X}{M}\right)} = 0.215 + \dfrac{C_e}{22}$	0.97
	Langmuir non-linear	$\dfrac{X}{M} = \dfrac{(19.8)(0.26)(C_e)}{1 + 19.8C_e}$	0.87

Eqs. (1) and (2) represent the non-linear and linearized forms of the Freundlich isotherm respectively, that were used in this study.

$$\frac{X}{M} = KC_e^{1/n}. \tag{1}$$

$$\log\left(\frac{X}{M}\right) = \log(K) + \frac{1}{n}\log(C_e). \tag{2}$$

The following non-linear and linearized forms of the Langmuir isotherm were also used in this study.

$$\frac{X}{M} = \frac{abC_e}{1 + bC_e}. \tag{3}$$

$$\frac{C_e}{(X/M)} = \frac{1}{ab} + \frac{C_e}{a}. \tag{4}$$

The adsorption of phenol on peat and bentonite was described well by the Freundlich isotherm (Table 6 and Figs. 3 and 4), whereas the Langmuir isotherm was found to better describe the adsorption of phenol on fly ash (Table 6 and Fig. 5). Peat, fly ash and bentonite were found to adsorb 46.1%, 41.6% and 42.5% phenol respectively from an initial concentration of approximately 1000 μg/l. The low removal efficiencies for the adsorption of phenol observed in this study was due to the fact that phenol was in competition with organics (BOD) for the sorption sites. Results from the batch adsorption studies showed that peat, fly ash and bentonite desorbed 18.4%, 15.2% and 30.9% of adsorbed phenol respectively.

The adsorbability of phenol by these adsorbents is 0.015 to 0.1 mg phenol per gram of adsorbent, generally much lower than that of activated carbon which has an adsorption capacity of 0.161 g phenol per gram of activated carbon [1]. A comparison of
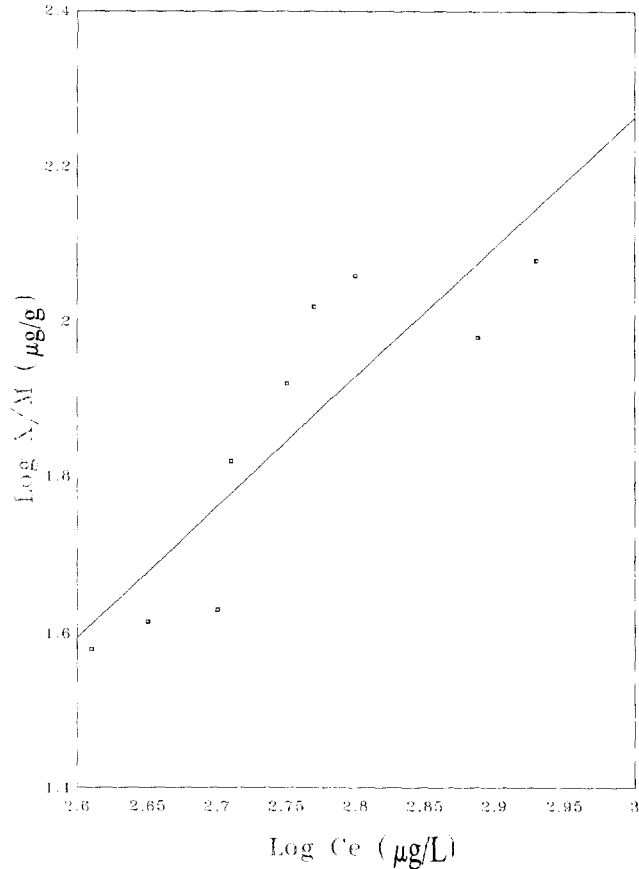
Fig. 3. Fruendlich isotherm for phenol adsorption on peat at $21 \pm 1°C$.

Freundlich K values for phenol adsorption by these adsorbents (4.6×10^{-4} $\mu g/g$ for peat and 5.1×10^{-11} $\mu g/g$ for bentonite) with the K value for activated carbon adsorption of phenol (111 mg/g) shows that the adsorption capacities of peat and bentonite were relatively low.

From the (X/M) values it is deduced that the phenol adsorption capacity follows this order: peat > fly ash > bentonite. At relatively acidic pH, the phenol molecule is at its molecular state, being adsorbed by physical forces. Nevertheless, the exchangeable protons can protonate the phenol molecules, these then being adsorbed by ion exchange. Peat is a complex material containing lignin and cellulose as major constituents. The aromatic nature of the lignin base structure is similar to the structure of phenol molecule [3]. It is likely that the aromatic surfaces of the lignin polymer serve to sorb the phenol molecule while the cross-linking side chains serve to 'trap' and hold the phenol molecule in place. The intermolecular distances and area within the lignocellulosic polymer could also be suitable for the phenol molecules to be 'absorbed' between basal
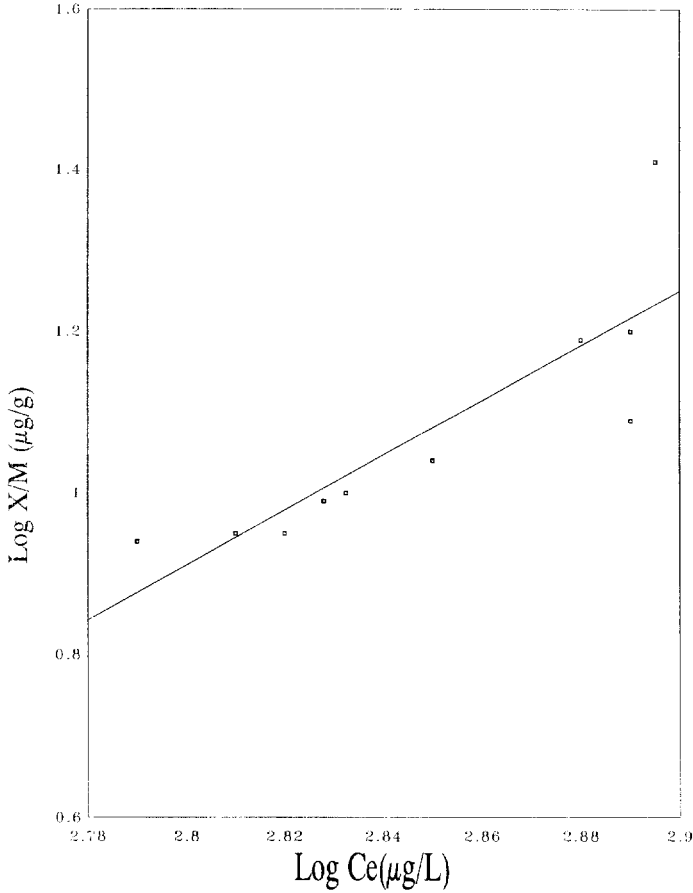
Fig. 4. Fruendlich isotherm for phenol adsorption on bentonite at $21 \pm 1°C$.

lignin units. The sorption mechanism in this regard may be a combination of the aforementioned mechanisms and cannot be attributed to either one specifically. The controlling factors for such competing mechanisms would ultimately be the inter- and intra-molecular forces between the lignin and the phenol molecules.

An important fact to be considered is the relatively high solubility of phenol in water. At the conditions under which the batch adsorption experiments were conducted, it seems that phenol molecules compete with water molecules for the montmorillonate (bentonite) interlayer surfaces. Thus, adsorption takes place only on the external surface.

Alumina (Al_2O_3) and silica (SiO_2) are the major constituents of fly ash. Structurally, silica is described as composed of SiO_4 tetrahedra in which each oxygen atom is shared between two adjacent tetrahedra. The Si–O bond is around 50% ionic due to the large difference in the electronegativity of oxygen and silicon [4]. Thus, it should be capable of adsorbing considerable amounts of phenols, which are polar molecules. This is
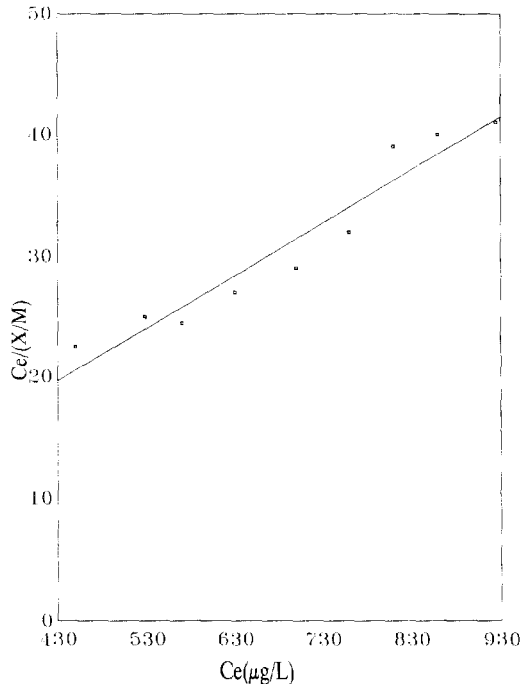
Fig. 5. Langmuir isotherm for phenol adsorption on fly ash at $21 \pm 1°C$.

supported by the appreciable adsorptive capacity of fly ash as demonstrated by the present results. Molecular weight, solubility and polarity of the compound has significant effect on the adsorption mechanism(s). These parameters act simultaneously during the process and hence, the effect is a combined one. Studies conducted by Banerjee et al. showed that the following trends take place during the sorption process: (1) adsorption increases as the molecular weight of the compound increases; (2) non-polar compounds are removed more easily than polar compounds; and (3) fly ash favoured adsorption of low water soluble compounds [5].

4. Application to practice

The results of the study can be used to design batch adsorption systems for the removal of phenol. Such a batch system will be applicable to small industries generating phenol-containing wastewater. The adsorbent can be added to the wastewater collected in a tank and the mixture agitated for the equilibrium time found from this study. The amount of the adsorbent can be obtained from the isotherm data. The liquid can then be decanted and discharged. Because of low pH, adjustment of pH is necessary before discharge to a sewer or water course. The used adsorbent has to be suitably disposed of.

5. Conclusions

Results of the study showed that peat, fly ash and bentonite can adsorb phenol to the extent of 40–45% when contacted for a period of 16, 5, and 16 h respectively in the pH range of 4 to 5. Detailed economic analysis would be required in any evaluation of these adsorbents.

Acknowledgements

References

[1] J.R. Perrich, Activated carbon adsorption for wastewater treatment, CRC Press, Boca Raton, FL, 1981.
[2] Standard Methods for the Examination of Water and Wastewater, American Public Health Association, New York, NY, 1990.
[3] A.D. Cohen, M.S. Rollins, W.M. Zunic, J.R. During, Water Res. 25 (1991) 1047.
[4] S. Kumar, S.N. Upadhya, Y.D. Upadhaya, J. Chem. Technol. Biotechnol. 37 (1978) 281.
[5] K. Banerjee, P.Y. Horng, P.N. Cheremisinoff, M.S. Sheih, S.L. Cheng, Sorption of Selected Organic Pollutants by Fly Ash, Proceedings, 43rd Purdue Industrial Waste Conference, W. Lafayette, IN, published by Lewis Publishers, Boca Raton, FL, 1989.