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Adsorption of Phenol from Aqueous Systems onto Spent Oil Shale

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ABSTRACT

To evaluate its ability to remove phenol from aqueous solution, Jordanian "spent" oil shale, an abundant natural resource, has been used in an experimental adsorption study. Equilibrium of the system has been determined at three temperatures: 30, 40, and 55°C. The resulting experimental equilibrium isotherms are well represented by Frendlich, Langmuir, and Redlich–Peterson isotherms. The relevant parameters for these isotherms, as regressed from the experimental equilibrium data, are presented. Effects of solution pH (in the range of 3–11), in addition to effects of three inorganic salts (KI, KCl, and NaCl, each at 0.1, 0.01, and 0.005 M), on the equilibrium isotherms have been experimentally investigated. The effects of pH in the presence of KI and NaCl were also investigated for a possible interaction between salts and solution pH. The initial concentration of phenol in the aqueous system studied ranges from 10 to 200 ppm. Experimental results show that while an acidic solution has no effect on the adsorption capacity of spent oil shale to phenol, a highly basic solution reduces its adsorbability. No sound effect was observed for the inorganic salts studied on the adsorption of phenol on spent oil shale. The experimental results show that there is no interaction between the pH of solution and the presence of salts. In spite of its ability to remove phenol, spent oil shale showed a very low equilibrium capacity (of an order of magnitude of 1 mg/g). Should the adsorption capacity of the shale be improved (by different treatment processes, such as grafting, surface conditioning), results of this study will find a direct practical implication in serving as "raw" reference data for comparison purposes.

Key Words. Adsorption; Oil shale; Phenol; Salts; KCl; KI; NaCl; pH

INTRODUCTION AND LITERATURE REVIEW

Adsorption processes are widely utilized in chemical and petrochemical industries and are becoming increasingly attractive in biotechnology and environmental control engineering. Activated carbon is the most widely used material as an adsorbent due to its high surface area per unit mass. Since activated carbon is expensive, researchers try to utilize available naturally occurring materials.

The removal of phenolic pollutants, of which phenol is typical, is necessary because of its toxicity and slightly pungent odor. There are many methods to remove phenolic materials from aqueous solutions. In water treatment the most widely used method is the adsorption of phenol on the surface of active materials. In this work we try to use spent oil shale to adsorb phenol from aqueous solutions.

A literature survey indicates that there is growing interest in utilizing low-cost, naturally occurring adsorbents to remove trace organic materials from wastewater. Meyer et al. (1) used several low cost natural adsorbent materials including vermiculite, sawdust, barbecue charcoal, maize stalks, sand, rice husks, and peat moss to remove color from textile-plant effluents. More than 50% of the color was removed from the wastewater, with barbecue charcoal and rice husks showing the best adsorptive qualities (67 and 65%, respectively). Ackley et al. (2) summarized a review of the literature regarding the structure, composition, and ion exchange of clinoptilolite, as well as adsorption and diffusion in natural zeolite. Adsorption and diffusion in modified clinoptilolites have been related to the location of exchangeable cations and the corresponding effects of these cations upon channel blockage. These results suggest a much greater potential for separation of gas mixtures by natural zeolite than previously recognized. Takasaka et al. (3) studied the physicochemical properties and gas adsorption separation characteristics of Italian zeolite and its modified products. Rassokha and Avramenko (4) investigated the effect of adsorption modification of the surface of synthetic and natural zeolites on the properties of the fillers and furan–epoxy composites. Young et al. (5) used natural zeolite in dehydration processes. Abdel Wahhab et al. (6) used pressed olive seed residues to remove basic dyes from aqueous solutions. The adsorption capacity of such residues was found to be comparable to that of carbon, taking into consideration all economic aspects. Attili and Dwairi (7) evaluated Jordanian phillipsite tuff regarding its application in water softening to remove ammonium and toxic heavy metal ions. According to these authors, Jordanian phillipsite tuff showed high selectivity for the removal of Cd^{2+}, Cu^{2+}, and Cr^{3+}. Bino (8) used Jordanian zeolitic tuff as an ion exchanger for water treatment uses. Most recently, polymeric adsorbents were investigated for separating trace organics from aqueous systems. For example, Pilipenko et al. (9) used a series of porous polymeric sorbents and compared their adsorbability of phenol from aqueous solutions. Cooney and Wijaya (10) studied the adsorption of aromatic compounds having different numbers of acidic and/or basic ionizable groups onto activated carbon as a function of pH. Coughlin and Tan (11) studied the effect of adding 0.002 and 0.004 M $CaCl_2$ to solutions of sodium benzenesulfonate in contact with activated carbon. Jawaid and Weber (12) investigated the effects on sodium benzenesulfonate adsorption by a pelleted activated carbon caused by adding zinc chloride, calcium chloride, or potassium carbonate in the amount of 1 part salt per 100 parts charcoal. Randtke and Jepsen (13) reviewed the literature on salt effects on the adsorption of humic and fulvic acids onto activated carbon.

The present study is aimed toward experimental investigation of the effects of pH and three inorganic salts (NaCl, KCl, and KI) on phenol adsorption from dilute aqueous solutions onto Jordanian spent oil shale.

EXPERIMENTAL

All chemicals were research grade and were used without further purification. Spent oil shale was crushed and ground so as to pass through 0.212 mm mesh. Adjustment of pH was accomplished using an 85% phosphoric acid solution or a 30% sodium hydroxide solution. A digital pH meter (Microprocessor HI 8520), calibrated with standard pH solutions, was used for adjustment of the pH value.

A set of seven glass tubes was used to generate the needed data for each adsorption isotherm. Each tube was charged with a 50-mL solution of the same initial concentration of phenol but the amount of solid adsorbent differed from one tube to another, such that the final equilibrium data covered a range of concentrations from 10 to 200 ppm. The amount of solid adsorbent introduced ranged from 2 to 40 g per 50 mL of solution. A balance (Mettler AJ 100) with an accuracy of 1×10^{-4} g was used in preparing the different weights. The set of tubes, tightly closed, was then shaken for sufficient time in a thermostated liquid bath shaker (Karl Kolb D-6072) where the temperature was maintained constant within ±0.1°C until equilibrium was attained, as reflected by the constancy of the concentration of phenol in the mixture. The solid adsorbent was removed by the combined effect of centrifugation and double filtration, and then a sample was withdrawn and analyzed for the equilibrium concentration of phenol in the liquid mixture. The method of analysis used here is the standard method adopted by Gales and Booth (14), which is based on spectrophotometeric analysis of the developed color resulting from the reaction of phenol with 4-aminoantipyrine. Reproducibility was ensured by repeating the experiment under the same conditions.

A calibration curve relating the concentration of phenol in an aqueous system to the absorbance, using a Spectronic 21 UVD spectrophotometer, was then used to find the concentration of phenol in the samples. The amount of phenol adsorbed at equilibrium per unit mass of solid adsorbent is found from a simple materials balance:

$$q_e = V(C_0 - C_{eq})/M$$

where C_0 and C_{eq} are the initial and the equilibrium concentrations of phenol in solution, respectively, V is the volume of the liquid mixture, and M is the mass of spent oil shale.

RESULTS AND DISCUSSIONS

Three different isotherms (30, 40, and 55°C) were generated experimentally to explain the effect of temperature on the adsorption of phenol on oil shale. The equilibrium adsorption capacity of the adsorbent is increased by decreasing the equilibrium temperature, as shown in Fig. 1. For example, when the equilibrium concentration of phenol is equal to 100 ppm, the amount of phenol adsorbed on oil shale is 0.46, 0.39, and 0.32 mg/g at 30, 40, and 55°C, respectively. This behavior is expected for physical adsorption which is exothermic in nature in most cases.

The experimental adsorption isotherms are well described by Langmuir, Freundlich, and Redlich–Peterson equilibrium models. The constants of

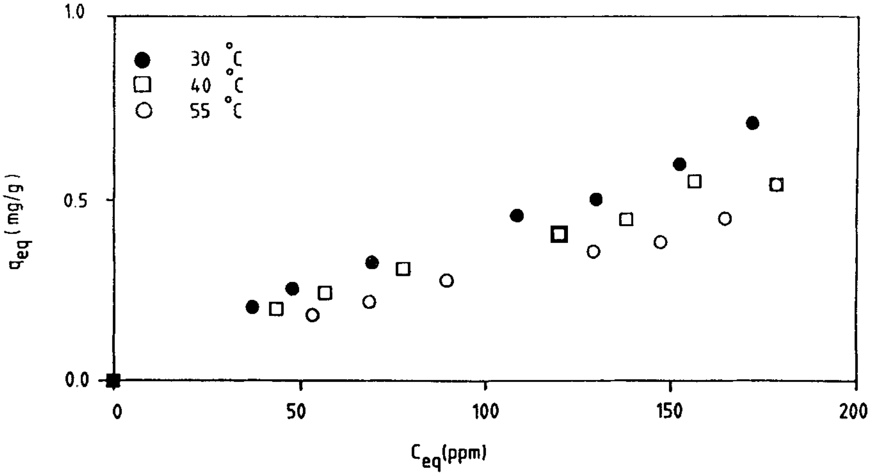

FIG. 1 Adsorption isotherms for phenol onto oil shale in aquous systems.

TABLE 1
Constants of Langmuir, Freundlich, and Redlich–Peterson Isotherms for the Adsorption of Phenol on Spent Oil Shale

Temperature (°C)	Langmuir: $q = (AC)/(1 + BC)$		Freundlich: $q = KC^N$		Redlich–Peterson: $q = (\lambda C)/(1 + \beta C^{\mu})$		
	A	B	K	N	λ	β	μ
30	0.005	0.001	0.011	0.807	0.149	13.41	0.198
40	0.005	0.003	0.012	0.746	0.096	7.602	0.262
55	0.003	0.000	0.005	0.896	0.047	9.001	0.111

Langmuir, Freundlich, and Redlich–Peterson models are obtained by regressing the experimental data, using Marquardt's optimization algorithm (15). These constants are shown in Table 1.

The effect of solution pH on the adsorption equilibria of phenol on oil shale is shown in Fig. 2, where it is shown that a basic solution of pH 11 has the lowest adsorption capacity. A highly acidic solution (pH 3), on the other hand, increases the equilibrium adsorption capacity, but only slightly. No effect is observed for the case of pH 9, as is obvious in Fig. 2. These results are in agreement with the explanation advanced by Cooney and Wijaya (10) to explain the effect of pH on adsorption. Accord-

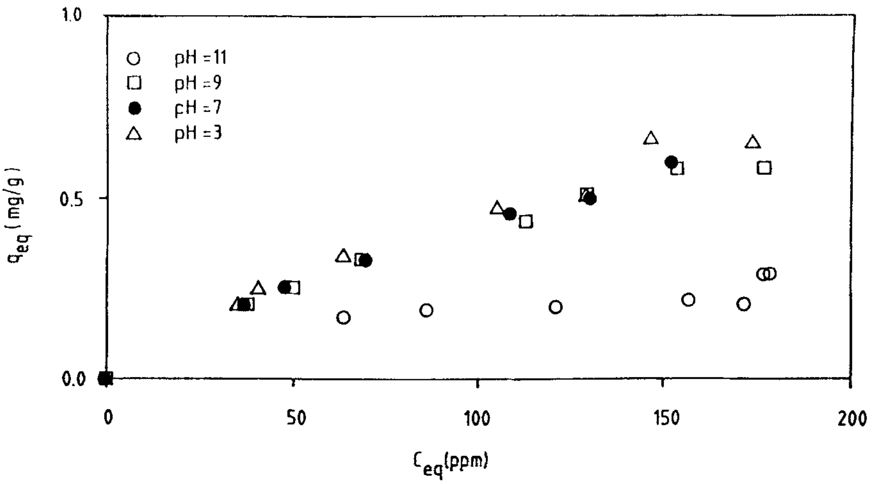

FIG. 2 Effect of pH on phenol adsorption onto oil shale at 30°C.

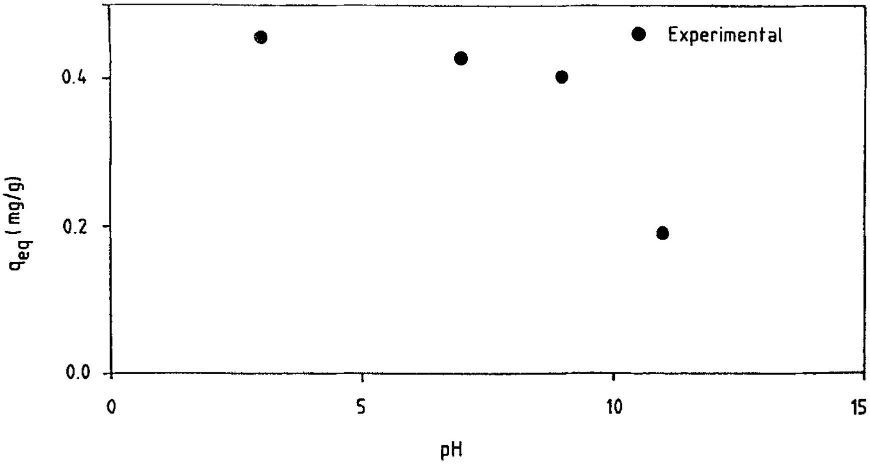

FIG. 3 Effect of pH on phenol adsorption onto oil shale for an equilibrium concentration of C_{eq} = 100 ppm phenol at 30°C.

ing to Cooney, phenol, which is a weak acid, will be adsorbed to a lesser extent at higher values of pH due to the repulsive forces between the adsorbed ions $C_6H_5O^-$ prevailing at higher pH values. Moreover, Cooney's explanation predicts that the pH of the solution will have a sound adverse effect on the adsorbability of the adsorbent at values greater than the pK_a of the adsorbate, which is around 10 in this case (16). This result is also clear from Fig. 3 (based on data of Fig. 2) which shows the effect of pH on the adsorbability of phenol on oil shale for an equilibrium concentration of 100 ppm. Clearly, below a pH of 9, the adsorbability of phenol is high and decreases slightly with the pH. As the pH rises above 9, the adsorbability falls sharply to much lower values, since the degree of ionization increases with pH.

Figure 4 shows that there is no major effect of potassium iodide (KI) on phenol adsorption on oil shale. As for potassium chloride, no effect is seen below a C_{eq} of about 120 ppm as is clear from Fig. 5. Beyond this concentration, it is seen from the same figure that a concentration of 0.01 M KCl in the solution reduces the equilibrium concentration of phenol. Figure 6 shows that sodium chloride, like potassium iodide, has no effect on the equilibrium adsorption capacity of shale toward phenol. However, it has been reported (10) that NaCl can enhance the adsorbability of benzoic acid on activated carbon. This is attributed to the partial nullification of repulsion forces between adsorbed ions. Since the adsorbing ingredient

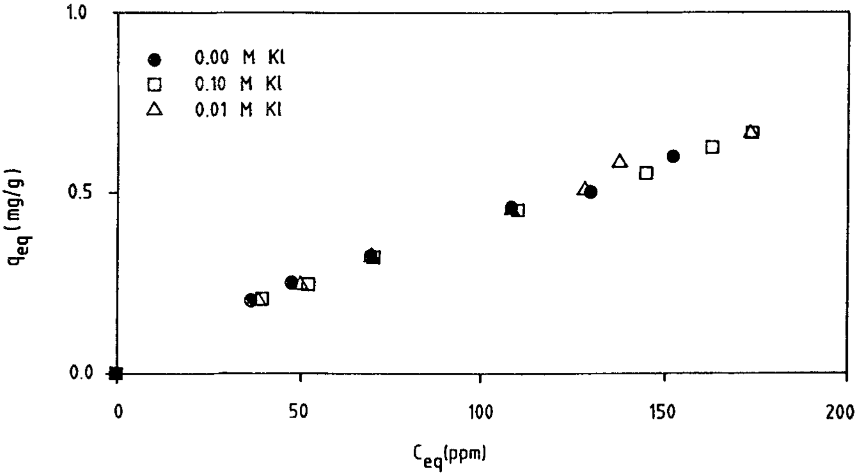

FIG. 4 Effect of potassium iodide (KI) on phenol adsorption on oil shale at 30°C.

in oil shale is very minute (as is clear from the low capacity of adsorption), the adsorbed ions are far from each other, and hence have a negligible effect on the salts.

To verify the interaction between the solution pH and the inorganic salts in their effect on the adsorption of phenol, experiments in which

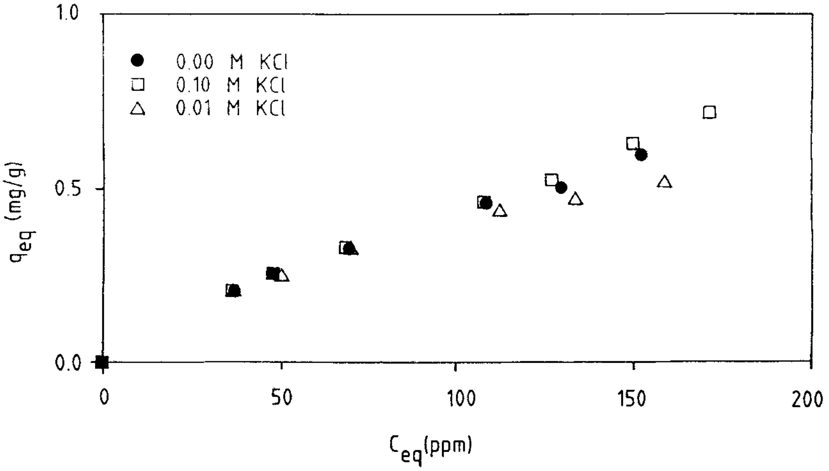

FIG. 5 Effect of potassium chloride (KCl) on phenol adsorption on oil shale at 30°C.

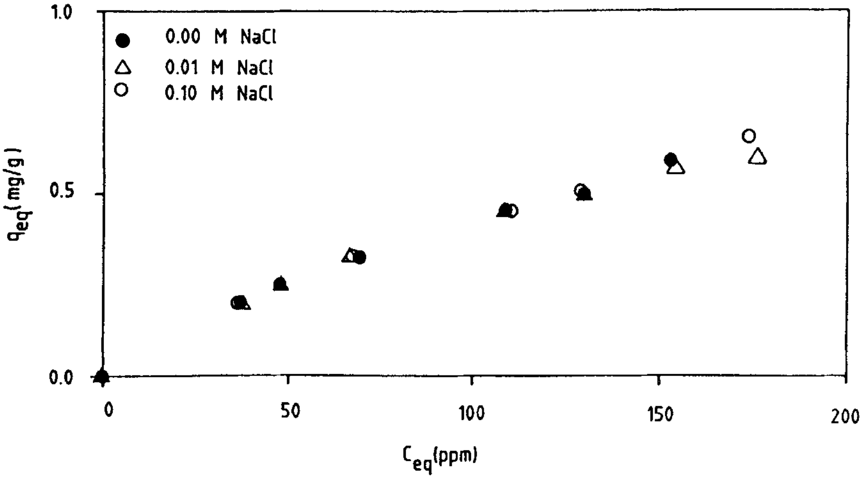

FIG. 6 Effect of sodium chloride (NaCl) on phenol adsorption onto oil shale at 30°C.

both the pH and the concentration of a certain salt were varied (Figs. 7 and 8) have been conducted. Comparison of the results of Fig. 7 with those of Fig. 2 shows that the effects of pH are unchanged by the presence of salt. At an equilibrium concentration of 100 ppm, for example, the

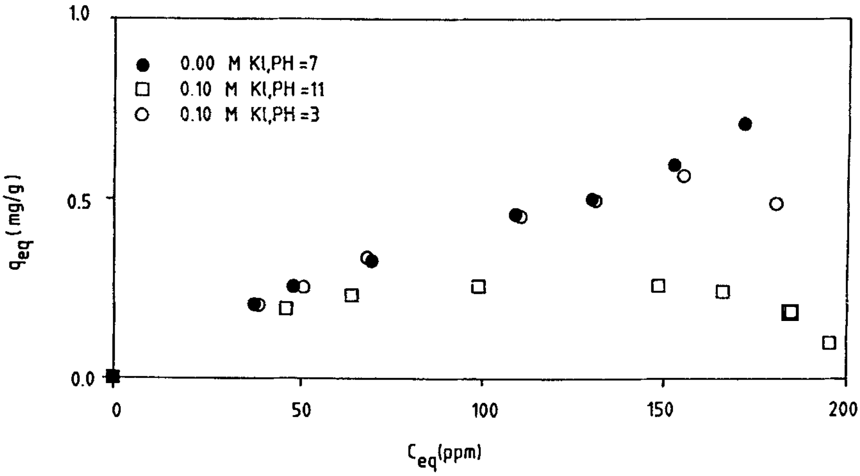

FIG. 7 Effect of pH on phenol adsorption onto oil shale at 30°C in the presence of potassium iodide (KI).

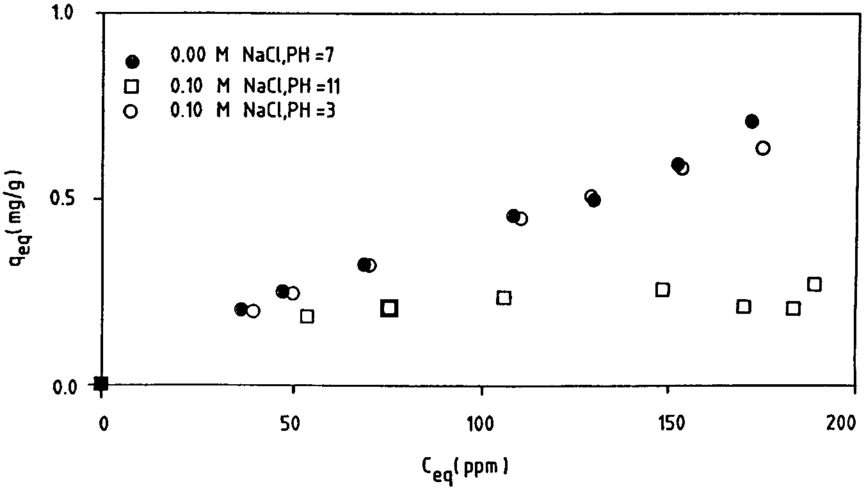

FIG. 8 Effect of pH on phenol adsorption onto oil shale at 30°C in the presence of sodium chloride (NaCl).

amounts of phenol adsorbed on oil shale at pH 11 were 0.19, 0.23, and 0.27 mg/g for 0 M salt, 0.1 M NaCl, and 0.1 M KI, respectively, as shown in Figs. 7 and 8. The apparent maximum in equilibrium adsorption, q_{eq}, for pH 11 and 0.1 M KI is an odd phenomenon that has been experimentally encountered in this study and for which no immediate answer is available. Figure 8 shows the effect of pH in the presence of NaCl salt. The presence of NaCl produces no additional changes in oil shale adsorbability, indicating no mutual interaction between the solution pH and the presence of sodium chloride.

CONCLUSIONS

The equilibrium isotherms of the adsorption of phenol on spent oil shale have been determined at 30, 40, and 55°C. The equilibrium experimental data have been fitted to Langmuir, Freundlich, and Redlich–Peterson equilibrium models, and the relevant parameters for these models have been determined. Effects of solution pH and three inorganic salts (KI, KCl, and NaCl) on the adsorption equilibria have also been investigated.

The experimental results show that acidic solution has no effect on the adsorption capacity of oil shale to phenol. Highly basic solution, on the other hand, reduces the adsorbability of oil shale. A minor effect was observed on phenol adsorption onto oil shale in the presence of inorganic salts. The experimental results show that there is a certain degree of coupling between the pH of a solution and the presence of KI salt. Other salts have shown no interaction with the solution pH. The experimental results are explained in terms of the degree of ionization of the adsorbate which is controlled by the pH of the solution.

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