Regeneration of Spent Earth by Wet Oxidation

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Regeneration of deoiled spent earth by wet oxidation has been investigated. Molecular oxygen was used as an oxidizing agent. Effects of operating parameters such as speed of agitation, temperature, oxygen partial pressure, slurry concentration, and cycle of regeneration have been studied. Kinetics of regeneration was found to be first order with substrate concentration and also with dissolved oxygen concentration.

Decolorization capacity of regenerated earth was the same as that of its virgin bleaching earth. Adsorption isotherm data was fitted in Freundlich equation. The values of Freundlich constants of regenerated earth were comparable with the values of virgin bleaching earth.

Natural/active Fuller's earth and activated carbon are widely used adsorbents in the vegetable oil industry. In view of reducing operating costs, various attempts have been made to desorb the adsorbed material from spent earth, to make it suitable for reuse (1-3). The methods generally used in the past include thermal, solvent and chemical regeneration. Wet oxidation, which falls into the category of chemical regeneration, is attractive because of its cleanliness, compactness and cost effectiveness over other processes.

Wet oxidation, often known as the "Zimmerman process," refers to the chemical reaction between molecular oxygen and suspended/dissolved organics in the presence of water at elevated temperature and pressure (4). The operating temperature varies over the range of 125 - 350°C and 1-20 MPa pressure. At high temperature, the oxidation reaction is fast enough to exploit it in practice. The reaction proceeds via fragmentation of large molecules into smaller molecules and finally oxidation to carbon dioxide and water. The process is being used for a variety of environmental control and energy related applications (5).

Charest and Chornet (6) reported wet oxidation of activated carbon. Effects of agitation speed, temperature and oxygen pressure have been studied. The oxidation proceeds readily with oxygen pressure as low as 4 MPa and at temperatures higher than 200°C. The reaction was found to be first order with respect to oxygen partial pressure. It was observed that the reaction takes place throughout the particle.

Gitchel et al. (7, 8) reported regeneration of spent carbon used in a variety of waste water treatment applications by wet oxidation. Chemical and physical tests of the regenerated carbon showed that wet oxidation retains all the adsorbate relative efficiencies and the pore structure of the virgin carbon with the exception of the smallest pore surface (≤ 10 Å in diameter). The effect of successive regeneration also was studied.

Natural coloring pigments in oils and fats are higher carbon chain organics like β-carotene, xyenthophyll, chlorophyll and others. As all these compounds are

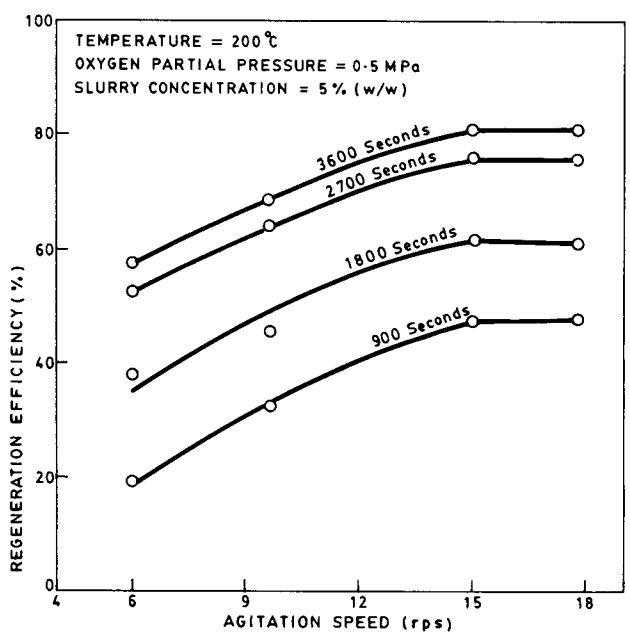

FIG. 1. Effect of speed of agitation on regeneration efficiency.

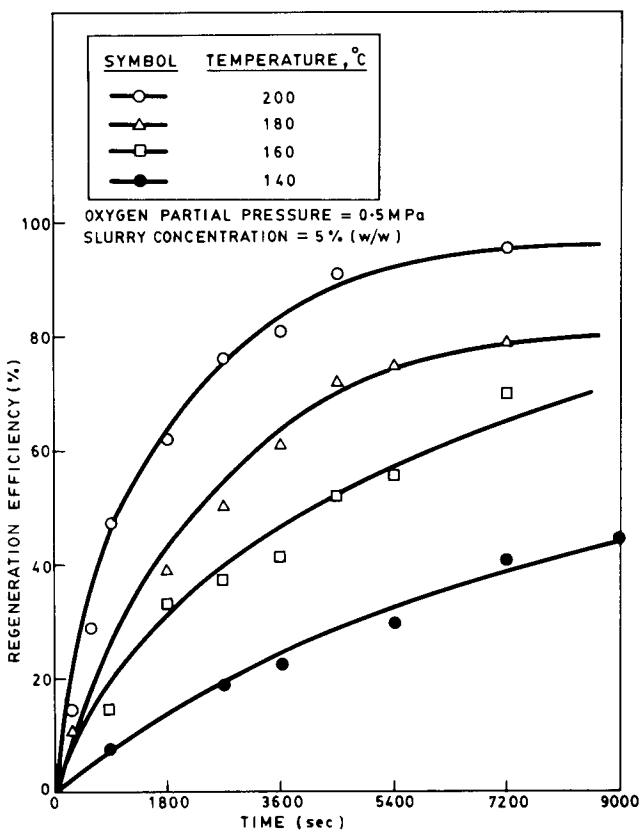

FIG. 2. Effect of substrate concentration on regeneration efficiency.

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sensitive to oxidative degradation, it was hypothesized that the wet oxidation method would be useful for regeneration of spent bleaching earth.

MATERIALS AND METHODS

Spent earth (86% bleaching earth, 14% activated carbon) was taken from a commercial vegetable oil refinery which had been refining peanut oil. The bleaching clay consisted mainly of aluminosilicate minerals.

Bleachability was tested on refined peanut and cottonseed oils to check regeneration efficiency on a moderately colored and highly colored oil. Bleachability testing was done in a similar experimental set-up as reported by Kheok (9). Additional arrangements were made to introduce bleaching earth in the bleaching pot under vacuum. Testing was carried out at 85°C ± 1°C with 1% bleaching earth for peanut oil and at 92 ± 1°C with 2% bleaching earth for cottonseed oil. Bleaching was done under pressure of 5-10 mmHg. The time of 35-40 min was found to be sufficient to get the extent of bleaching near its equilibrium value. Oil color was measured by a Lovibond tintometer, Model E. The regeneration efficiency was calculated on the basis of reduction in red color. Results were compared with virgin bleaching earth containing the same ratio of bleaching earth and activated carbon as in spent earth. The results of regeneration efficiency of bleaching earth on cottonseed oil were used for finding the kinetics. Regeneration efficiency (RE) of regenerated earth was calculated by

$$RE = \frac{B_R}{B_V} \times 100 \quad [1]$$

where B_R is the bleachability of regenerated earth (percent) and B_V is the bleachability of virgin earth (percent).

Adsorption isotherm data was obtained by treating the oil with different weight ratios of oil/bleaching earth. The adsorption isotherm data was fitted in the mathematical expression developed by Freundlich:

$$C = K C_e^{n} \quad [2]$$

where C is the concentration of adsorbates/g of adsorbent at equilibrium (Lovibond red unit/g); K is the decolorizing power constant of the adsorbent; C_e is the oil phase equilibrium concentration of adsorbate (Lovibond red unit), and ^{n} is the decolorization sensitivity constant toward the range of concentration of the adsorbate.

EXPERIMENTAL

Deoiling of spent earth was done by the conventional solvent extraction method using a soxhlet apparatus. n-Hexane (60-80°) was used as solvent. Deoiled earth was dried at 110°C for four hr to remove traces of

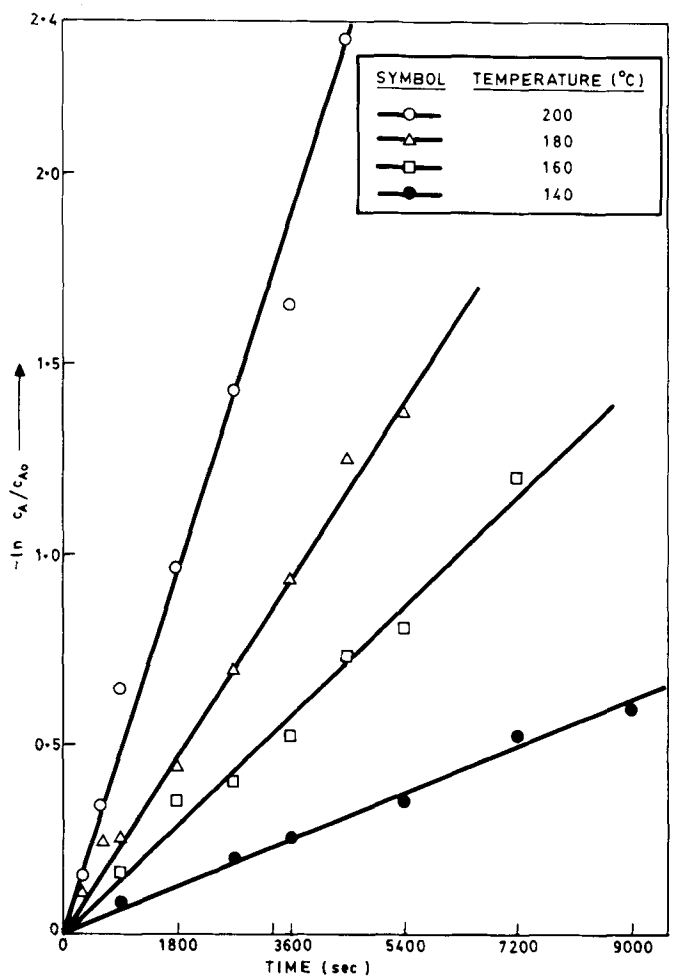

FIG. 3. Kinetics of regeneration with substrate concentration.

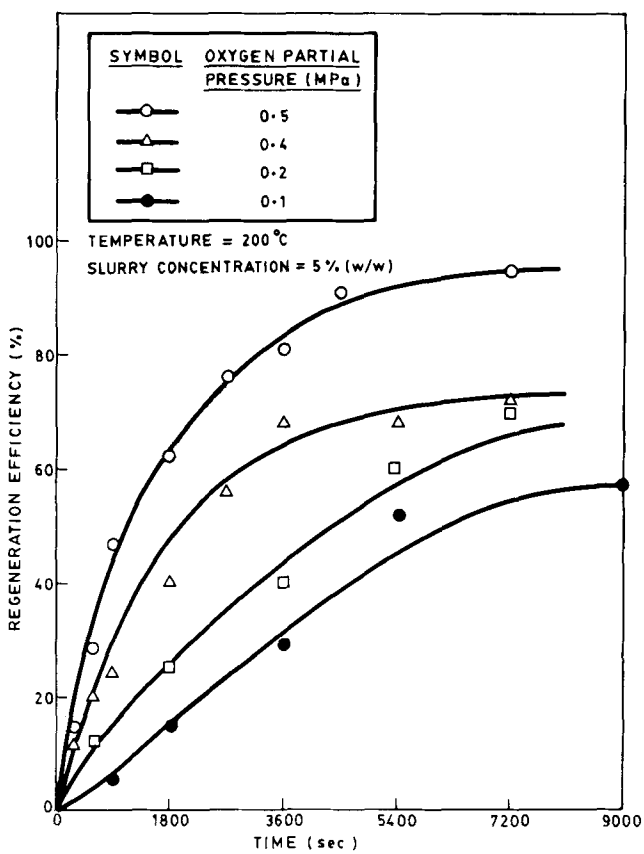

FIG. 4. Effect of oxygen partial pressure on regeneration efficiency.

solvent. Dried earth was used for regeneration. Regeneration was carried out in a two-l SS 316 autoclave equipped with an electrical heating jacket, gas inlet, gas outlet, pressure releasing valve and rupture disc. Mechanical agitation was provided by six-blade disc turbine impellers.

The autoclave was charged with 1000 cm^3 of the desired concentration of slurry, using distilled water as an aqueous phase. The stirring speed was adjusted as desired. A vacuum pump was used to evacuate air from the autoclave. The charge was preheated to the desired temperature. Oxygen from the cylinder was sparged into the autoclave directly beneath the impeller at the desired oxygen partial pressure. This time was considered as 'Zero' time for the reaction. Purging of gas was continued to maintain the desired oxygen partial pressure during the course of reaction. The temperature was maintained within ± 1°C of the desired temperature. Intermediate samples were withdrawn during the course of the reaction. The regenerated earth was pulverized to its original particle size (≤ 75 microns) and tested for bleachability. Periodic samples at higher slurry concentrations could not be withdrawn due to choking of the sample in the outlet line.

RESULTS AND DISCUSSION

The adsorbates on spent earth are carotenoids, soaps and other impurities. Carotenoids are unsaturated hydrocarbons, highly sensitive to oxidative degradation (10). Although these compounds are insoluble in water at atmospheric temperature, their desorption in aqueous phase at high temperature was observed. The reaction between organics and oxygen in the aqueous phase can be represented by

$$\text{Organic substrate} \rightarrow \underset{\text{weight compounds}}{\text{Lower molecular}} \rightarrow CO_2 + H_2O$$

Complete destruction of organics and desorption of non-oxidizable and partially oxidizable compounds into the aqueous phase revives the adsorbing efficiency of the adsorbent. Thermal regeneration also occurs, together with oxidative regeneration. Therefore, the studies on thermal regeneration were carried out separately (11).

The color of peanut oil in the 5.25″ cell was 27 yellow and 2 red, and of cottonseed oil in the one-inch cell was 42 yellow and 7.8 red. The bleachability of virgin bleaching earth was 80% on peanut oil and 57.7% on cottonseed oil.

TABLE 1

Reaction Rate Constants at Various Temperatures

Temperature (°C)	Rate constant (k) ($\frac{m^3}{kmole}$ sec^{-1})
140	1.66×10^{-2}
160	3.42×10^{-2}
180	5.0×10^{-2}
200	7.98×10^{-2}

Effect of speed of agitation. The effect of agitation speed was studied to ensure that all the mass transfer resistance was overcome and the true intrinsic kinetics was being investigated. Experiments were conducted at 200°C and oxygen partial pressure of 0.5 MPa. The slurry concentration was 5% (w/w) in all the experiments. The agitation speed varied over the range of 6-18.3 r/s. Results are plotted in Figure 1. The external mass transfer was eliminated at a speed higher than 15 r/s. Hence, all the additional experiments were conducted above 15 rps. Because the mass transfer resistance was eliminated at the highest temperature (200°C), it did not contribute any resistance at lower temperatures.

Effect of substrate concentration. Experiments were carried out in the temperature range of 140-200°C and at an oxygen partial pressure of 0.5 MPa. The slurry concentration was 5% (w/w) in all the experiments. The results are plotted in Figure 2.

TABLE 2

Reaction Rate Constants at Various Oxygen Partial Pressures

Oxygen partial pressure (MPa)	Rate constant (k′) (sec^{-1})
0.1	9.17×10^{-5}
0.2	1.64×10^{-4}
0.4	3.03×10^{-4}
0.5	5.19×10^{-4}

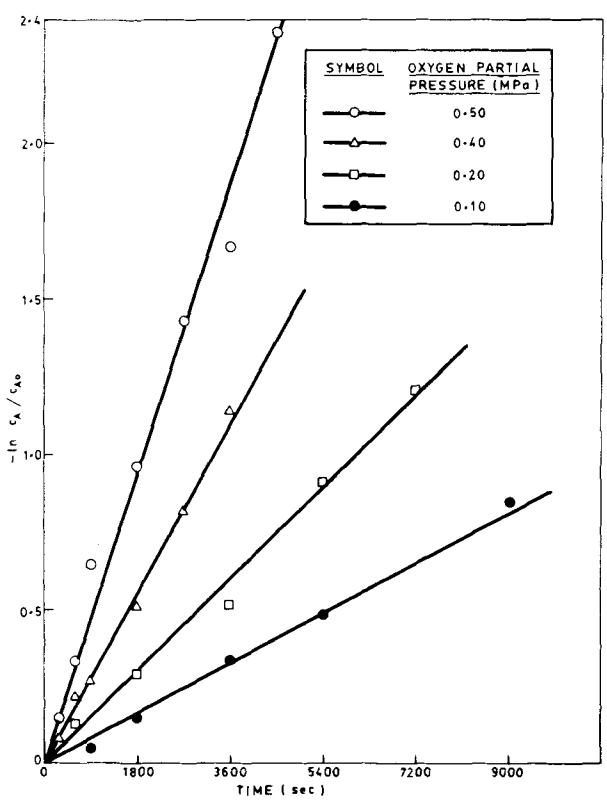

FIG. 5. Kinetics of regeneration with oxygen partial pressure.

The rate expression can be written as

$$\frac{dC_A}{dt} = k[C_A]^m[O_2]^{m'} \quad [3]$$

where C_A is the concentration of adsorbates on adsorbent in terms of percent deactivation; t is the time in seconds; k is the second order reaction rate constant ($\frac{m^3}{kmole}$ sec^{-1}); ^{m} is the order with respect to substrate concentration; $[O_2]$ is the concentration of dissolved oxygen in liquid phase (kmoles/m^3), and $^{m'}$ is the order with respect to dissolved oxygen concentration.

At constant oxygen partial pressure equation (3) can be written as

$$\frac{dC_A}{dt} = k'[C_A]^m \quad [4]$$

where C_A is the concentration of adsorbates on adsorbent in terms of percent deactivation; k' is the specific first order reaction rate constant (sec^{-1}), and ^{m} is the order with respect to substrate concentration.

where $$k' = k[O_2]^m \quad [5]$$

where k' is the specific first order reaction rate constant (sec^{-1}); k is the second order reaction rate constant ($\frac{m^3}{kmole}$ sec^{-1}); $[O_2]$ is the concentration of dissolved oxygen in liquid phase (kmoles/m^3), and ^{m} is the order with respect to substrate concentration.

From Figure 3 it can be seen that the order with respect to substrate concentration (percent deactivation) is first order. The specific rate constants were calculated by plotting - ln C_A/C_{Ao} (concentration of adsorbates on adsorbent in terms of percent deactivation/initial concentration of adsorbates on adsorbent in terms of percent deactivation) against time. The values of first-order rate constants are given in Table 1.

Effect of oxygen partial pressure. The effect of oxygen partial pressure was investigated over the range of 0.1 - 0.5 MPa and at 200°C. The slurry concentration in all the experiments was 5% (w/w). The extent of regeneration increases with an increase in the oxygen partial pressure. Results are shown in Figure 4. The rate constants were calculated by plotting - ln C_A/C_{Ao} against time, as shown in Figure 5. The values of reaction rate constants are given in Table 2. The reactio rate was found to be first order with respect to oxygen partial pressure. A plot of log k against log-dissolve oxygen concentration is shown in Figure 6. The order with respect to dissolved oxygen concentration was found to be first order.

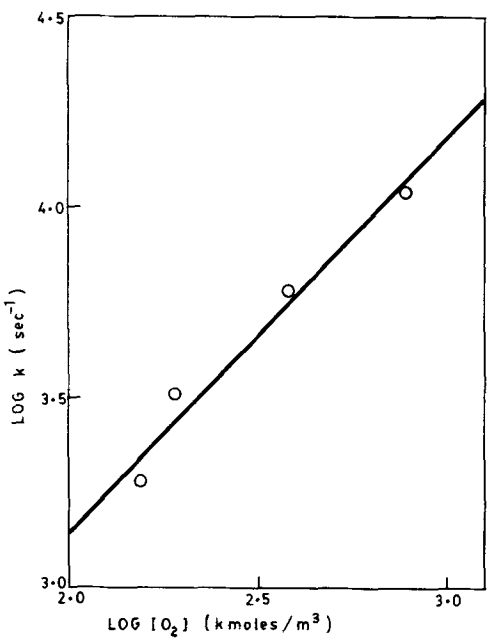

FIG. 6. Plot of log k versus log-dissolve oxygen concentration.

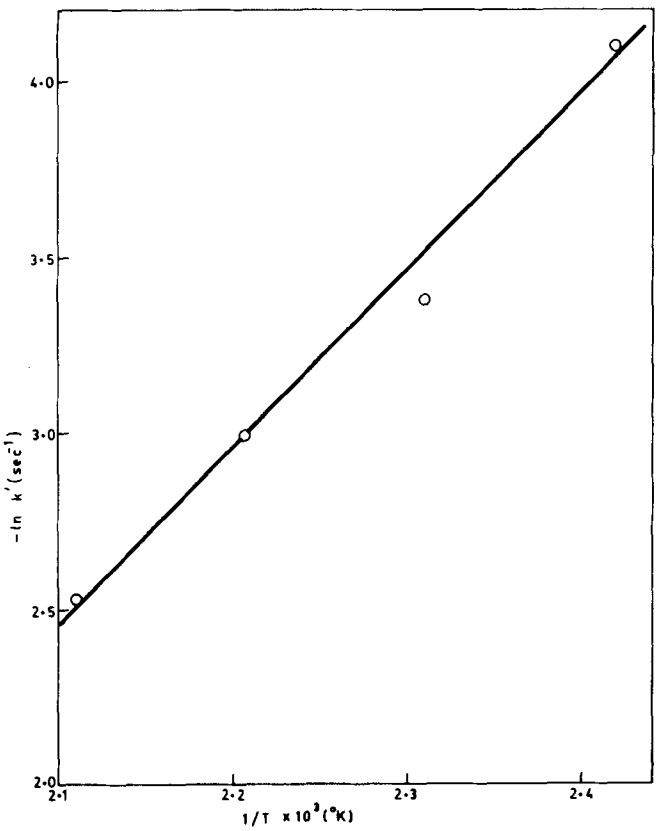

FIG. 7. Arrhenius plot of regeneration rate constants.

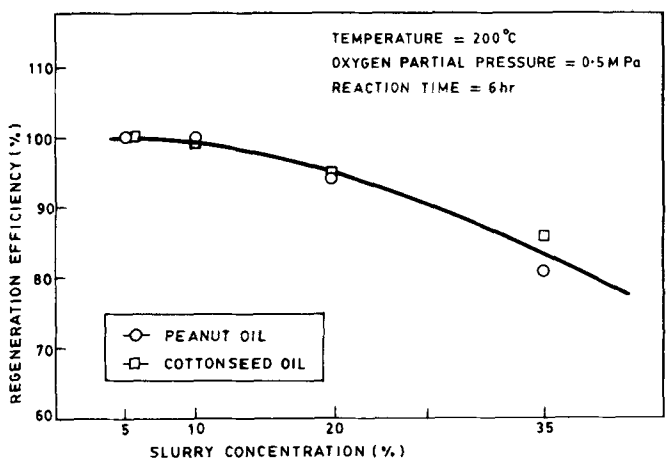

FIG. 8. Effect of slurry concentration on regeneration efficiency.

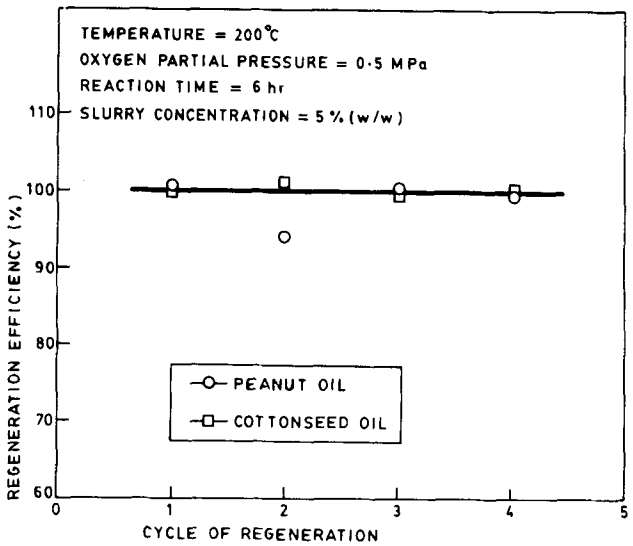

FIG. 9. Effect of decolorization efficiency on the cycle of regeneration.

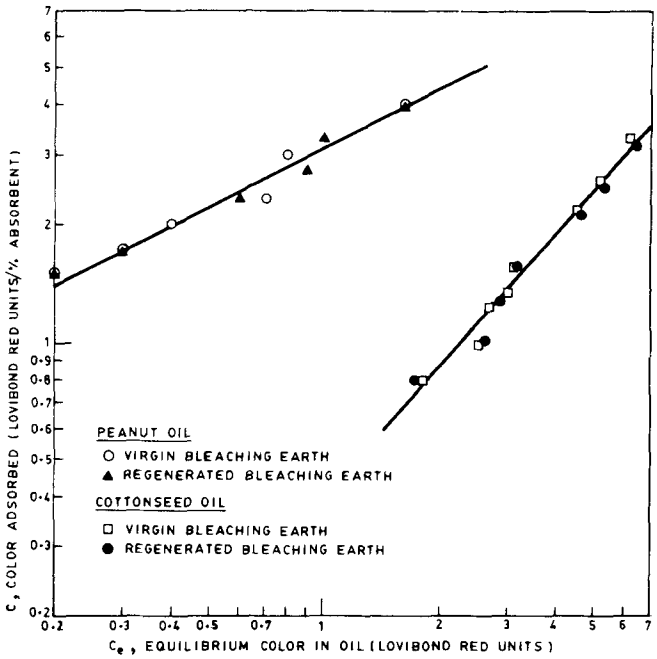

FIG. 10. Adsorption isotherm equilibrium plot for virgin and regenerated bleaching earth.

Effect of temperature. To find the dependence of reaction rate constant on temperature, the Arrhenius equation was used to find activation energy (Fig. 7). The value of apparent activation energy was found to be 10.0 kcal/gm mole.

Effect of slurry concentration. Experiments were conducted in a slurry concentration range of 5-35% (w/w). Regeneration was done at 200°C and 0.5 MPa of oxygen partial pressure for six hr. Results are shown in Figure 8. The extent of regeneration decreases with an increase in the slurry concentration. Only 80-82% regeneration was obtained at 35% slurry concentration. With an increase in solid loading the amount of adsorbates to be destroyed increases. Therefore, for a given reaction time, the extent of regeneration decreases. Complete regeneration was found even for 35% loading when the reaction time was 14 hr.

Effect of cycle of regeneration. Successive regeneration of spent earth was studied in order to use bleaching earth repeatedly. Results are shown in Figure 9. The extent of regeneration was found to be independent of the cycle of regeneration. The extent of regeneration was found to be 100% even after the fourth cycle. Further, the regenerated earth works well on both types of oil. In the oxidative regeneration process, probably no degraded products accumulate on the surface of the adsorbent, unlike aqueous phase thermal regeneration.

Adsorption equilibria. Adsorption isotherms of virgin and regenerated earth (after the first cycle of regeneration) on peanut and cottonseed oils are shown in Figure 10. The values of K and n for virgin and regenerated earth were found to be similar. This indicates that, apart from the revival of adsorption capacity, the basic nature of bleaching earth remains unchanged during the regeneration process. The Freundlich equations for virgin and regenerated earth for peanut and cottonseed oils, respectively, are represented by the following equations:

$$C = 3.12\ C_e^{0.50} \quad [6]$$

$$C = 0.32\ C_e^{1.5} \quad [7]$$

where C is the concentration of adsorbates/g of adsorbent at equilibrium (Lovibond red unit/g) and C_e is the oil phase equilibrium concentration of adsorbate (Lovebond red unit).

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