Regeneration of Spent Earth in Aqueous Medium

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A simple method of regeneration of spent earth at a relatively low temperature has been developed. Deoiled spent earth was regenerated in the form of a slurry using water as an aqueous phase, in the temperature range of 170–270°C. The effects of temperature, slurry concentration and cycle of regeneration have been studied. An attempt has been made to discern the controlling mechanism.

Regenerated earth from the present method does not impart any malodor to the oil as against thermally regenerated earth.

Bleaching of vegetable oils by adsorption is widely practiced for the removal of color bodies, residual traces of soap and other impurities present in the neutralized oil. These impurities which adsorb on the surface of the adsorbent are responsible for deactivating the adsorbent. Desorption destruction of these impurities can result in revival of the activity. The popular adsorbents are natural and active fuller earths and activated carbon. Typical characteristics of adsorbents are given in Table 1. Spent bleaching earth contains about 20–40% oil. The recovery of oil and the reuse of spent bleaching earth are the areas where great opportunity exists for cost saving in the oil processing industry.

TABLE 1

Characteristics of Adsorbents

	Natural earth	Activated earth	Activated carbon
pH (suspension in water)	7–8	3–6	5–9
Apparent bulk density (g/cm^3)	0.65–0.90	0.35–0.70	0.35–0.60
Specific surface area (m^2/g)	75–130	150–350	500–1300
Particle size (80%) (micron)	< 75	< 75	< 75
Moisture content (%)	8–16	8–15	8 max

Kaufmann and Mukharjee (1) have reviewed the different methods for recovery of oil from spent earth. Recovery by water separation and solvent extraction are commonly discussed. Numerous processes have been proposed for the regeneration of spent earth. These methods are either complicated or costly; thus, they are not often used. It is a general practice to recover the fatty matter from an earth and discard the deactivated earth (2).

Fuege and Janssen (3) have described solvent regeneration of spent earth. Organic solvents such as acids, alcohols, ethers, ketones, etc., were used. A low molecular weight ketone was found to be the most effective solvent. Regeneration could be done up to 96–97%. Effect of successive regeneration was also studied. Degree of regeneration was reduced to about 79–80% after 20 cycles.

Kuck et al. (4) have reported thermal regeneration of spent alumina used for bleaching of cottonseed oil. Regeneration was done at 400–700°C, followed by remoisturizing the earth (to at least 10%). In this method, about 98–99% regeneration was achieved. Successive regeneration has not affected the extent of regeneration even after 15 cycles. Thomopoulos and Liapis (5) have reported chemical regeneration. Earth was treated with an aqueous solution of 0.4% anionic detergent and 2% tripolyphosphate for the removal of residual oil; then, the oxidation of coloring matters was done by Cl_2, $KMnO_4$ or $K_2Cr_2O_7$. Many other processes for the regeneration have been patented, and these are summarized in Table 2.

Regeneration of spent carbon is well reported in the literature, which includes thermal, solvent, chemical and biological methods. Loven (6) has described the various methods for the regeneration of activated carbon including the economic aspects of regeneration. However, there is practically no attempt in the published literature regarding the mechanism and kinetics of regeneration processes.

In the present study, deoiled spent earth has been regenerated at a relatively lower temperature and in an

TABLE 2

Summary of Patented Literature on Regeneration of Spent Earth

Authors	Pretreatment	Regeneration method
Gerhard, S., et al. (7)	Solvent extraction and steaming	Heat treatment at 500–550 C in presence of air.
Hermann, M. (8)	Solvent extraction	Heat treatment up to 450 C under vacuum
Sethuraman, V., et al. (9)	Extraction with organic solvents	Heat treatment at 400–600 C
Werner, B. (10)	Washing with hydrocarbon	Heat treatment at 350–500 C followed by treatment with HCl.

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aqueous medium. Kinetics of the process has also been studied to generate useful design data.

MATERIALS AND METHODS

Spent earth (86% activated fuller earth, 14% activated carbon) was taken from a vegetable oil refinery, which was used for bleaching peanut oil. Bleaching earth consists mainly of alumino-silicate minerals. Bleachability was tested on neutralized peanut oil in an experimental set-up similar to that reported by Kheok (11). Additional arrangements were made to introduce bleaching earth into the bleaching vessel under vacuum. The test was carried out at 86 ± 1°C, with 1% bleaching earth, under pressure of 5–10 mmHg. The time, 35–40 min, was found to be sufficient to get the extent of bleaching practically to its equilibrium value. The color of oil was measured by Lovibond tintometer, Model E, using a 5.25″ cell. Percent regeneration was calculated on the basis of reduction in red color only. Results were compared with virgin bleaching earth containing the same ratio of bleaching earth and activated carbon. The color of neutralized peanut oil was 27 yellow and 2 red. The bleaching efficiency of virgin bleaching earth was found to be 80%.

Adsorption isotherm data was obtained by treating the oil with different weight ratios of bleaching earth.

EXPERIMENTAL

Extraction of oil from spent earth was carried out in a Soxhlet apparatus. n-Hexane (60–80°C) was used as solvent. After complete extraction the earth was dried at 110°C for six hr to remove traces of solvent.

Regeneration of the dried earth was carried out in a two-l S.S. 316 autoclave equipped with electrical heating jacket. Mechanical agitation was provided by six-bladed disc-turbine impellers. The gas inlet, gas outlet valve, pressure gauge and safety rupture disc were situated at the top of the head. A schematic diagram of the experimental set-up is shown in Figure 1. The spent extracted earth was treated in form of slurry. Distilled water was used as an aqueous phase. The autoclave was charged with one l of the desired concentration of slurry. The stirring speed was adjusted to keep all the particles in suspension. Air was evacuated from the autoclave using a vacuum pump. The charge was heated to the desired temperature. The time taken for heating varied from 30–40 min. The time at which the desired temperature was reached was taken as the zero time. The reaction was carried out for six hr. During the course of the reaction, temperature was maintained within ± 1°C of the desired temperature. Intermediate samples were withdrawn during the reaction when the solid loading was 5%. Samples were filtered, and the earth was dried. Regenerated earth was pulverized to its original particle size (<75 micron) and tested for bleachability. Intermediate samples at higher slurry concentration could not be withdrawn because of a choking problem in the sample outlet line.

RESULTS AND DISCUSSION

Treatment of spent earth in aqueous phase at higher temperature involves the regeneration process of solvent and thermal regeneration simultaneously. First, higher temperature increases the solubility of adsorbed species into the aqueous phase. This results in desorption of adsorbates into the liquid phase where the water acts as a solvent. Second, heat sensitive adsorbates undergo thermal degradation. Though the desorption of adsorbate in batch solvent regeneration is limited because of mutual solid/liquid desorption equilibria, simultaneous thermal degradation of adsorbate causes continuous desorption of adsorbates into the aqueous phase by mass action. This lowers the solid/liquid desorption equilibria value to where thermal destruction occurs.

Regeneration was carried out in the temperature range of 170–270°C (Fig. 2). The degree of regeneration

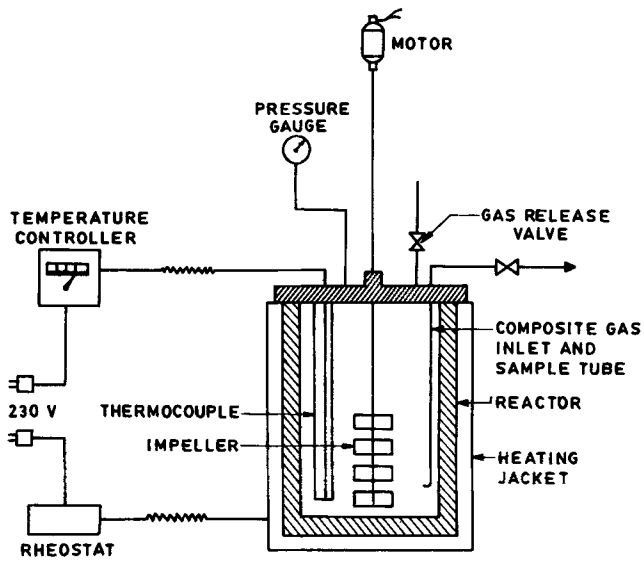

FIG. 1. Experimental set-up.

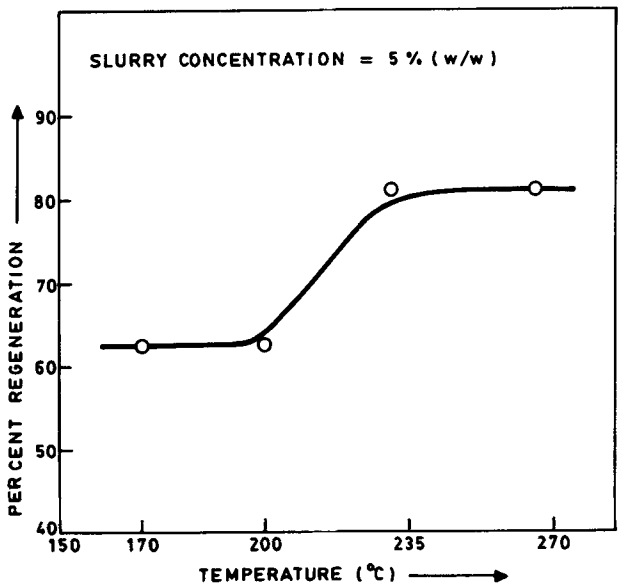

FIG. 2. Effect of temperature.

increases with an increase in temperature. About 81% regeneration was achieved at 235°C. Further increase in temperature has practically no effect on the extent of regeneration. Higher temperatures lead to thermal degradation of β-carotene (which is the main constituent of coloring bodies) into volatile and nonvolatile compounds (12). The release of volatile compounds and the desorption of water-soluble adsorbates in aqueous phase from adsorbing surface result in reactivation. Perhaps formation of nonvolatile products which retain on the adsorbent limits the regeneration beyond 81%.

It may be noted that some regeneration occurs during preheating. As a result, 31.2% regeneration was observed during the preheating period. Additional regeneration was found to follow a first order rate equation (Fig. 3). The rate constants at different temperatures are given in Table 3. The value of activation energy was found to be 3.9 Kcal/g•mole, by using the Arrhenius equation.

The mechanism of regeneration can be explained in four steps: (i) Desorption of adsorbate from the surface of the adsorbent; (ii) Intraparticle diffusion within pores to the outer surface of the adsorbent; (iii) Mass transfer from adsorbent to liquid bulk, and (iv) Possible degradation of adsorbate in liquid bulk. The observed value of activation energy is very low (3.9 Kcal/g•mole) for an intrinsic chemical reaction. It indicates that the process is not controlled by chemical reactions. In order to find the effect of external mass transfer, the value of mass transfer coefficient at reaction condition was calculated by using Hale's correlation. The diffusivity was calculated by the Wilke-Change equation considering β-carotene as an adsorbent (13). The mass transfer coefficient was calculated for particle sizes of 25, 50 and 75 microns. The true mass transfer coefficient worked out to be 0.25 ± 0.03 cm/s and the particle size had a negligible effect. Effective solid-liquid interfacial area was estimated using the following equation.

TABLE 3

First Order Rate Constants at Various Temperatures

Temperature (°C)	Rate constants (sec^{-1})
170	4.15×10^{-5}
200	5.63×10^{-5}
235	7.41×10^{-5}

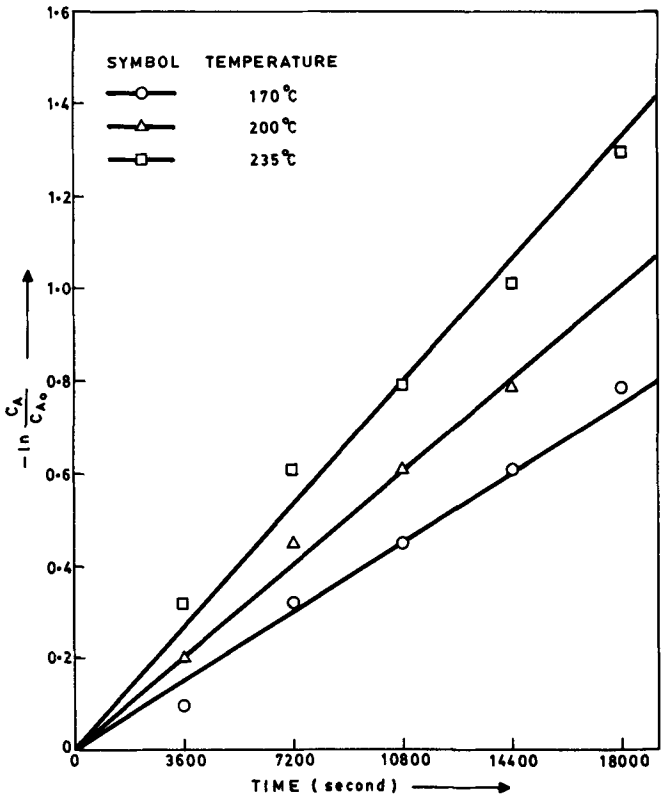

FIG. 3. First order kinetics of regeneration.

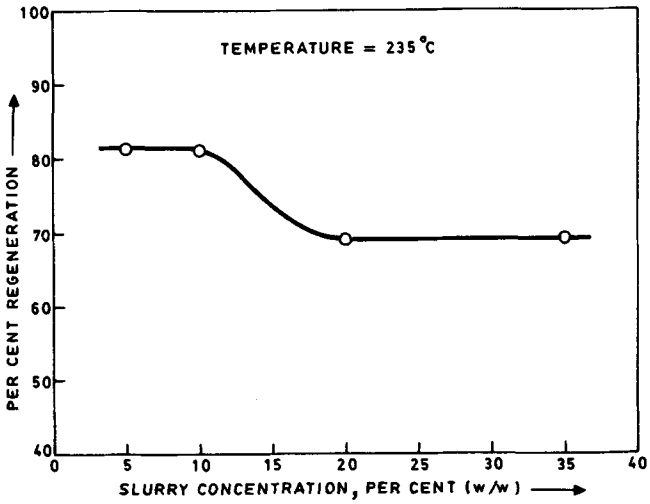

FIG. 4. Effect of slurry concentration.

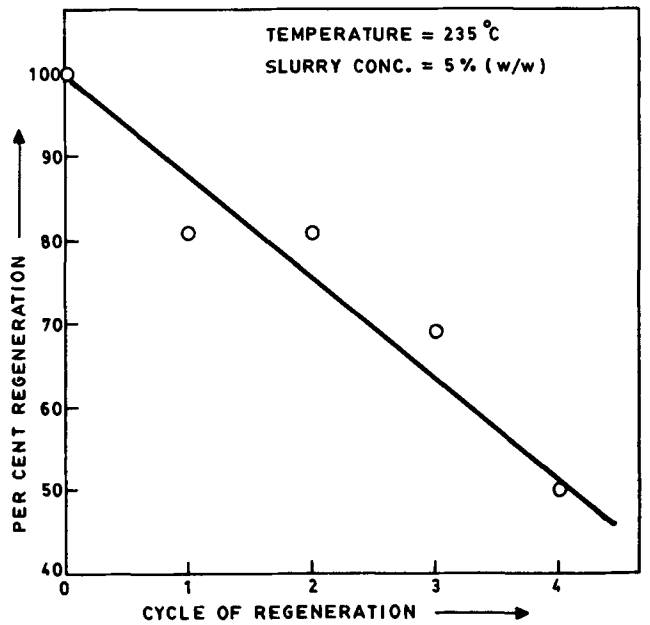

FIG. 5. Effect of cycle of regeneration.

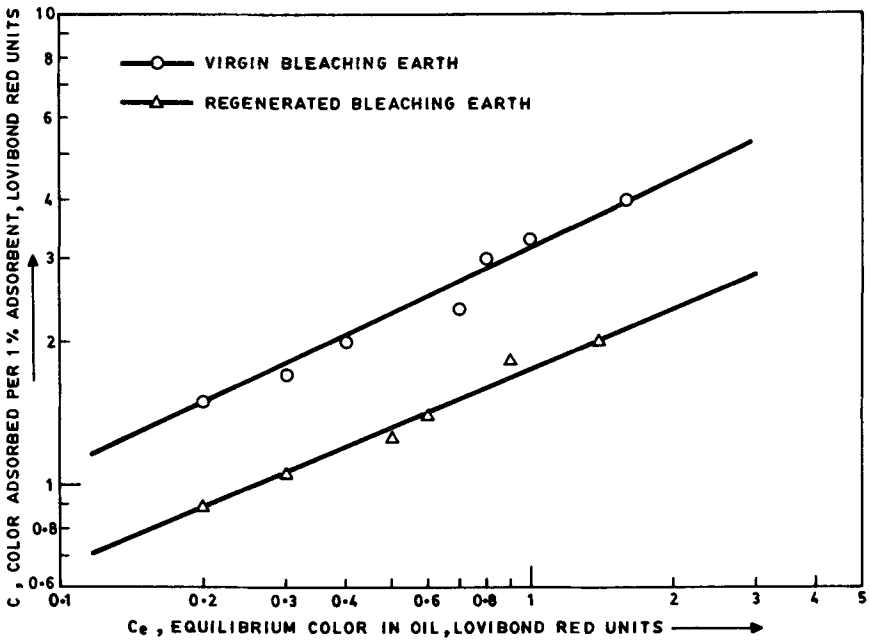

FIG. 6. Adsorption equilibria of peanut oil on bleaching earth.

$$a = \frac{6\,\varepsilon_s}{d_p} \qquad [1]$$

where a is the effective solid-liquid interfacial area in cm^2/cm^3, ε_s is the fractional solid hold-up and d_p is the particle size in cm.

For a 2% fractional solid hold-up (5% by weight) and a 50-micron particle size, the value of a is 2.4 cm^2/cm^3. Therefore, the overall mass transfer coefficient is 0.6 sec^{-1}. This means the solid-liquid mass transfer rate is relatively very fast and the regeneration half-life time should be on the order of seconds. For complete regeneration, the time required may be on the order of a few minutes, if the overall process is mass transfer controlled. Because the experimental investigation required more than three hr, it appears that solid-liquid mass transfer resistance does not exist.

From the foregoing discussion it appears that the regeneration process is controlled by the combined effect of desorption and internal diffusivity.

The effect of slurry concentration was studied in the range of 5 to 35% (Fig. 4). An increase in slurry concentration decreases the extent of regeneration, and only 69.0% regeneration was obtained at 35% slurry concentration. The reduction in the extent of regeneration with an increase in the solid loading may be due to the higher solid/water ratio. It is likely that the desorbed products will have higher concentration in water when the loading is increased. These compounds are likely to have some equilibrium adsorption relationship with the earth. This may become the controlling parameter at higher solid/water loadings.

Successive regeneration has been investigated, and the results are plotted in Figure 5. A systematic decrease in the extent of regeneration was observed with an increase in the number of regeneration cycles. Only a 50% regeneration was obtained after the fourth cycle. As explained earlier, 80–82% regeneration is possible in each cycle, which results in 50% regeneration after the fourth cycle.

Because thermally regenerated earth usually imparts malodor to bleached oil, the use of thermally regenerated earth is limited to the bleaching of industrial oils and fats (2). Though regeneration by aqueous phase regenera- tion is limited, the resulting regenerated earth does not impart any malodor to bleached oil and thus can be used for processing of edible oils and fats.

ADSORPTION EQUILIBRIA

Adsorption isotherm data of virgin and regenerated earth after the first cycle of regeneration are shown in Figure 6. The adsorption isotherm data was fitted in the mathematical expression developed by Freundlich.

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

where C is the concentration of adsorbate/g of adsorbent at equilibrium in Lovibond red unit/g, C_e is the oil phase equilibrium concentration of adsorbate in Lovibond red unit, and K and n are constants.

Equations (3) and (4) are the Freundlich equation for virgin and regenerated earth, respectively.

$$C = 3.18\,C_e^{0.47} \qquad [3]$$

$$C = 1.74\,C_e^{0.42} \qquad [4]$$

A lower value of constant K for the regenerated earth indicates lower bleaching capacity. The values of

the constant n, which shows the sensitivity of adsorption to concentration, were found to be practically the same for virgin and regenerated earth. This shows there is no change in the basic nature of bleaching earth during regeneration.

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