ACTIVATION AND CLARIFYING PROPERTIES OF FULLER'S EARTH.

Part VI. Adsorption of colouring matter by Fuller's Earth in Decolorisation of Oils.

By B. S. Kulkarni and S. K. K. Jatkar.

INTRODUCTION.

Although it is recognised that fuller's earth is one of the most powerful adsorbents both in aqueous and non-aqueous media, the true nature of its adsorptive action has not yet been the subject of a systematic study. The general belief of most of the workers is that surface and capillary effects must be the basic reason for the adsorptive action. Neumann and Köber (Angew. Chem. 1929, **40**, 337) found that in decolorisation of vegetable oils and oil-solutions of organic colours, the shape of the bleaching curves obtained with German earths conformed to the Freundlich adsorption isotherm. Similar findings are reported by Kobayashi and Yemamoto (J. Soc. Chem. Ind. Japan, 1930, **11**, 428-430) while working with various petroleum distillates, and also by Schultze (Angew. Chem. 1936, **49**, 74-77) in the course of his study of dehydration of bleaching earths. Physical adsorption has been assumed throughout Eckart's studies of the bleaching earth (Eckart and Wirzmuller, Die Bleicherde 1925, and also Eckart's many other papers on the subject in Z. angew. Chemie and Seifensieder Zeitung).

The lack of stoichiometric relations between the adsorbent and the adsorbate, the independence of reaction on the variable composition of the earth and on temperature and the adsorbability of apparently chemically unreactive substances, all point to purely physical adsorption. There are, however, a number of facts to indicate that chemical effects are not negligible. Langmuir (J. Amer. Chem. Soc., 1918, **40**, 1361) has emphasised the chemical features of adsorption pointing out that atoms and molecules on the solid surface do not necessarily lose their chemical reactivity. Stadnikoff (Kolloid-Z. 1922, **31**, 19) while distinguishing between various types of adsorption mentions 'chemical adsorption' which can be quantitatively expressed by the laws of mass-action. Folge and Olin (Ind. Eng. Chem. 1933, **25**, 1069) postulated a simultaneous adsorption and zeolitic action, the earth acting as *calcium zeolite*. The previous studies of the present authors have shown that there is an intimate relation between the hydrogen exchangeability of the earth in aqueous medium and its activation and decolorising power in vegetable oils, that montmorillonite structure is essential for activity and that the decolorising power mostly depends on the earth acting as hydrogen zeolite.

Whether the various adsorptive and chemical effects observed both in aqueous and non-aqueous media can be included under the term of adsorption and whether any of them conform to the Freundlich conception of adsorption is a question which requires further examination. Although the problem is complicated by the possibility of the earth acting differently in aqueous and non-aqueous media, it cannot be denied that there must be many common and correlative features of the behaviour of the earth in various media. The correlation of the different properties of the earth in various media requires systematic investigation in each medium with different earths. An attempt has been made in the present investigation to study the nature of adsorption of the colouring matter in oil by some of the activated Indian Fuller's earths.

EXPERIMENTAL.

Method.—The method of study proposed was to follow the decolorising effect when increasing quantities of the activated earths were stirred with an oil sample in which colour concentrations were also varied. The earths used for decolorisation were the same as described in the previous Parts: Jodhpur Earths I, II and III, Local Earth IV, C. P. Earth V, which were previously activated by digestion with hydrochloric acid and sieved through a 100-mesh sieve. The coloured oil used was a sample of acid-free safflower oil from Bijapur having about 16.7 Lovibond units of yellow colour.

The previous experiments of colour measurements were made with Lovibond Tintometer. It was found that, when using white light, a close linear relationship existed between the logarithms of the Lovibond numbers and the percentage of the original colour, which could be expressed by an equation

$$L_1 - L_2 = e^{Kc_1} - e^{Kc_2}$$

where L is the Lovibond number, c, the concentration and K is a constant. Our previous results showed an inverse proportionality between the bleaching value and the pH of the extract obtained by shaking the earth with sodium chloride solution.

Oil samples of various colour concentrations were prepared by mixing a known volume of coloured oil with colourless groundnut oil.

Decolorisation :—The decolorising experiments were carried out carefully by stirring a definite volume of the oil mixture with a weighed quantity of the earth at 90-95°. After stirring for fifteen minutes the oil was filtered hot. The time intervals for heating, decolorising and filtering were kept uniform.

Colour estimations :—Preliminary experiments of colour-measurements with Lovibond Colorimeter showed that the mesurements were too rough to be used for satisfactorily testing the adsorption isotherm. The desired degree of accuracy was therefore secured by using Pulfrich Photometer. The method consisted in finding the comparative intensities of transmission through the test sample, of light of suitable wavelengths, and through the same thickness of the original oil. The following table gives the intensity variations for different wave-lengths (obtained by means of light filters) where absorption was possible. The intensities are expressed as per cent. of the total intensity of transmission through the colourless oil.

It will be seen from the results (Table I) which are shown graphically in Fig. 1, that of the three suitable wave-lengths, viz., 4300 Å, 4700 Å and 5000 Å, the last gives the maximum variation of intensity with concentration. 4700 Å was unsuitable for matching, while 4300 Å gave better match than 5000 Å, in which the transmission was very feeble. 5000 Å was therefore used for higher colour concentrations while 4300 Å was used for the lower ones.

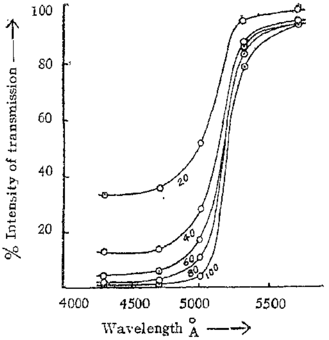


Fig. 1.

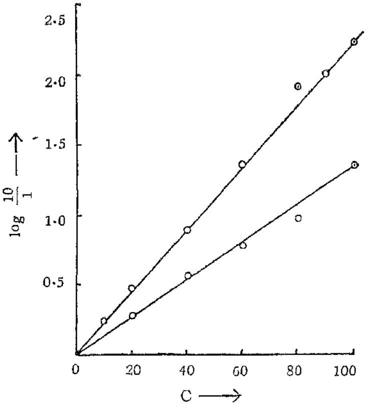


Fig 2.

TABLE I.

Intensities of Transmission for different Wave-lengths.

Colour concentration in the oil	4300 Å	4700 Å	5000 Å	5300 Å	5700 Å
10	57.96	...	...	...	...
20	33.40	35.20	51.50	95.50	nearly100
40	12.90	13.50	28.00	88.50	95.6
60	4.50	5.40	17.00	83.00	95.1
80	1.21	2.30	10.75	82.00	94.0
90	0.96	...	...	...	...
100	0.57	0.73	4.60	79.50	93.5

Secondly, it was necessary to ascertain whether the transmission of these wave-lengths through the oil mixture obeys the Beer-Lambert's Law, i.e., gives constant extinction coefficients. That the law is obeyed is shown from the constancy of K in Table II, calculated from the equation

$$KC = \log I_o/I \quad \dots \quad (1)$$

where K is the extinction coefficient, C is the colour constant and I_o and I are the intensities of transmission through the same thickness of the colourless and coloured oil samples respectively.

The concentration of colour in any desired sample of oil was calculated by substituting in the above equation the mean value of K and the factor log I_o/I, as directly read from the photometer drum.

TABLE II.

Extinction coefficients for 4300 Å and 5000 Å.

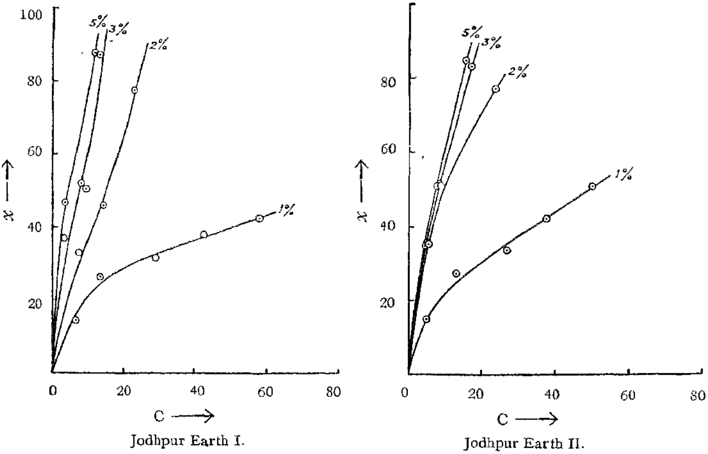
Colour Concentration in the oil.	4300 Å		5000 Å	
	log I_o/I	K	log I_o/I	K
10	0.237	0.0237	...	...
20	0.476	0.0235	0.268	0.0134
40	0.890	0.0224	0.551	0.0138
60	1.347	0.0224	0.770	0.0128
80	1.917	0.0239	0.770	0.0121
90	2.016	0.0224	...	...
100	2.242	0.0224	1.350	0.0135
		mean = 0.0230		mean = 0.0131

Results:—The colour estimations of the oil mixtures after decolorisation by various earths are given in Figs. 3 (A, B, C). In one set of experiments the quantity of the earth used was 1% by weight of the oil mixture while the colour-concentrations of the oil mixture were varied. In the other set, oil samples having different colour concentrations were treated with 1%, 2%, 3% and 5% earths. These gave the necessary data for the Freundlich Isotherm

$$x/m = a\, c^n \qquad \dots \qquad (2)$$

$$\text{or} \quad \log x = n \log c + \log a + \log m \qquad \dots \qquad (3),$$

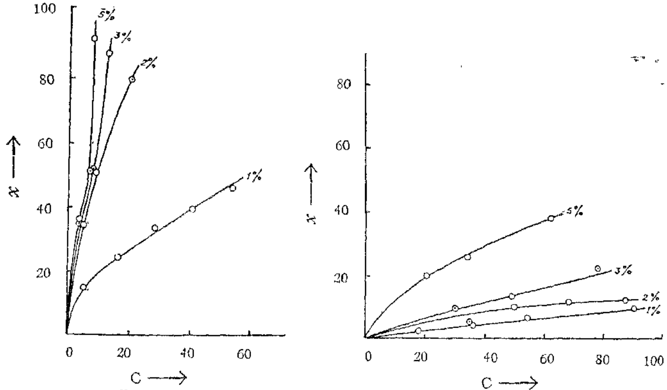
where x is the per cent. quantity of the colour removed, c the per cent. quantity of the colour remaining, m is the weight per cent. of the earth used and a and n are constants. The relations between the various values of x and c after correction for the small amount of colour in the colourless oil, are shown graphically in Figs. 3(A,B,C).



Jodhpur Earth I.

Jodhpur Earth II.

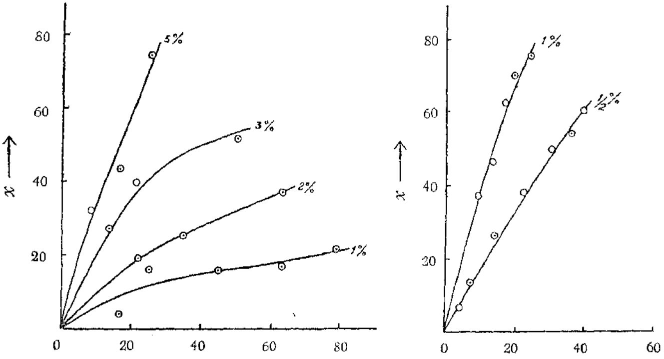
Fig. 3a.



Jodhpur Earth III

Local Earth

Fig. 3b



C. P. Earth

Jodhpur Earth (150-mesh.)

Fig. 3c.

In order to study the effect of increased surface on colour removal and on the adsorption equation, another set of decolorisation experiments was carried out with earth II, which was passed through 150-mesh. The following table gives the values of C and x and their relation is illustrated in Fig. 3(C).

TABLE III.

Jodhpur Earth II (150-mesh).

Original colour %	1/2 %			1 %		
	c	x (obs.)	x (cal.)	c	x (obs.)	x (cal.)
100	39.8	60.2	61.0	24.4	75.6	76.2
90	36.0	54.0	55.6	19.9	70.1	64.2
80	30.2	49.8	47.5	17.1	62.9	55.9
60	22.3	37.8	36.1	13.4	46.6	45.3
40	13.8	26.2	23.8	9.3	30.7	33.1
20	7.8	12.2	14.6	7.0	13.0	(26.1)
10	3.7	6.3	7.9	...	...	...

Discussion of the results:—In the foregoing results and the accompanying figures, the relations between the amount of colour removed, the colour retained and the weight of the absorbent have been brought forth over a considerably wide range of concentrations. Considering the relation between c the equilibrium colour concentration and x, the amount adsorbed, it is found that the curves show a sharp inflexion indicating two distinct portions. The three Jodhpur earths which are highly active, appear to fall in the same group, while the C. P. earth which has the lowest activity behaves entirely differently (cf. c—x curves). In the case of Jodhpur earth, the quantity of the colour removed is not at all proportional to the weight, while in the case of the C. P. earth, the lack of proportionality is markedly shown in experiments with lower proportion of the earth.

The relation between log c and log x instead of being linear according to equation (3) give curves which show a clear tendency to bend in the region of the higher or lower values of concentration, and this is more pronounced in some earths than in others. Similarly, for different proportions of the adsorbent (m) it is found that the spacings of the curves are not what should be expected from equation (3) and are found to differ from earth to earth. The values of a and n are thus not constant but change both with the nature of the earth and its weight and also with the concentration of the colour in the oil. The results obtained with finer earths did not show any improvement.

Although these results do not lead to a precise quantitative expression for the process of colour removal, the nature of the c−x curves and the close relationship between the hydrogen content of the earth and its activity, sufficiently justify the conclusion that in addition to adsorption effects, a major portion of the colouring matter undergoes chemical combination with the zeolitic hydrogen of the earth. To express the total effect a modification of the Freundlich equation of the form

$$x/m = a\,c^{n} + b\,c, \text{ a and b being constants,} \quad \ldots. \quad (4)$$

where the additional factor b c takes into account the decolorisation by chemical effect, is found to be suitable. It is found, however, that in the case of coarse ground earths, the equation is not applicable over the whole range of concentrations studied. Physical adsorption appears to predominate at low colour concentrations. Chemical effects on the other hand, mainly appear to operate with high concentrations. In the intermediate range both effects super-impose giving a pronounced bend in the c−x curves. In the finely ground earth, one may reasonably expect a simultaneous operation of the two effects over the whole range of colour concentrations. On this assumption, the values of a and b were calculated in the case of 150-mesh Jodhpur earth. With average probable values of the constants, ($n = 0.5$, $a = 1.72$ and $b = 1.26$), the values of x were calculated according to equation (4) and are given against the observed values in table III. The fair agreement between the observed and calculated values of x strongly supports the above conclusions.

SUMMARY

A systematic study of the problem of removal of the colouring matter in vegetable oil by various Indian fuller's earths has been made and the results have been explained in the light of the Freundlich isotherm.

It is found that although the relationship between the colour removed x and the colour remaining c appear to follow exponential curves, the various requirements of the Freundlich isotherm are not fulfilled. The law does not hold in the case of decolorisation (1) with higher and lower concentrations of the colouring matter, (2) higher concentrations of the active earth and (3) lower concentrations of the low grade earths.

It is suggested that although some of the colouring matter is removed by purely physical adsorption, the remaining probably forms definite chemical combinations with exchangeable hydrogen of the earth.

Department of Pure and Applied Chemistry,
Indian Institute of Science,
Bangalore, India.

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