OLIVE SEEDS EXPRESSION RESIDUES SUBSTITUTES FOR BASIC COLOUR REMOVAL

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ABSTRACT

Removal of basic dyes from aqueous solutions was carried out using prepared olive seeds expression residues. Some factors affecting the adsorption process were studied with the main objective of testing the feasibility of such a residue as an adsorbent. This work ought to be of a double reasoning; on one hand, this specific use for residues must decrease the area required for their disposal if not burnt, and, one the other hand, it may be a mean to decrease the amounts of imported active carbon or allied expensive adsorbents usually used. The adsorption capacity of such residue was found to be comparable to that of carbon taking into consideration all economic aspects. Langmuir isotherm was found to represent data much better than that of Redlich-Peterson; an equation of the following form was derived by least squares regression analysis of the data:

$$q_e = (5.085\ C_e)/(1+0.0564\ C_e) \qquad \text{(at 30°C)} \qquad (1)$$

with a correlation coefficient of 0.996. The energy of activation of the adsorption process was to be 4300 J/mole. The results obtained are encouraging to begin other trials not only by using other abundant agricultural residues and wastes, but also by using actual industrial effluents.

NOMENCLATURE

- A Langmuir model constant, l/mg
- A' Redlich-Peterson model constant, $(l/mg)^{\beta}$
- C Dye concentration in solution at time t, mg/l
- C_0 initial dye concentration in solution, mg/l
- C_e dye concentration in solution at equilibrium with q_e, mg/l
- K Langmuir model constant, l/g
- K' Redlich-Peterson model constant, l/g
- M mass of adsorbent, g
- m mass of adsorbent per unit volume, g/l
- q_e dye concentration in adsorbent at equilibrium with C_e mg dye/g adsorbent
- R gas constant, J/mole.°K
- x amount of dye adsorbed, mg
- ΔH heat of adsorption, J/mole
- β Redlich-Peterson model constant,----
- λ wave length of the day, nm

INTRODUCTION

Activated carbon is the most widely used material as an adsorbent, due to its high surface area per unit mass [1,2]. Its use in water and sewage treatments is of primary importance, besides its wide activity in adsorbing many organic compounds. Yet, the international price of activated carbon is going further and further up, thus needing the availability of further substitutes to maintain treatment costs as low as possible. Activated alumina, silica gel and molecular sieves may be considered as known substitutes of somewhat lower efficiency and thus of higher relative total costs.

Agricultural residues and wastes such as peat [3], wood saw-dust [4], bagasse [5] and Gift (olive seeds expression residues) [6], were found to be of acceptable efficiency for adsorbing colours from aqueous solutions and effluents and thus they have been thought-upon to be an activated carbon substitute of local abundance in most countries. The prices of such materials are very low compared with other carbon substitutes and their economic competition

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Table (1). Langmuir and Redlich-Peterson for Adsorbent Size 500-710 μm.

Temp. °C	A	K	A′	K′	β
20	0.0409	3.142	0.0446	3.203	0.9875
30	0.0554	5.085	0.0159	3.723	1.164
50	0.0360	3.987	0.00225	2.957	1.472

where K, A, K′, A′ and β are constants. A plot of C_e/q_e versus C_e will give a straight line of slope A/K and an intercept of 1/K for Langmuir isotherm as shown in Figure (4). The values of K′, A′ and β in Redlich-Peterson isotherm were evaluated by nonlinear regression analysis of the experimental data. The values of the constants in both models are shown in Table (1).

5. Batch Studies

Some parameters were chosen to represent, as far as possible, the feasibility of olive seeds expression residues for basic colour removal from aqueous solution. These were carried out based on the experimental fact that the only existing colour in the dye is that of the basic type. Acid dyes were discussed elsewhere, using the same adsorbent [6]. Actually, and on an industrial scale, mixtures of those dyes will be present in effluents. The parameters chosen were: the agitation efficiency, the ratio of adsorbent mass to the adsorbate volume, the initial dye concentration and the particle size of the adsorbent.

i. Initial concentration

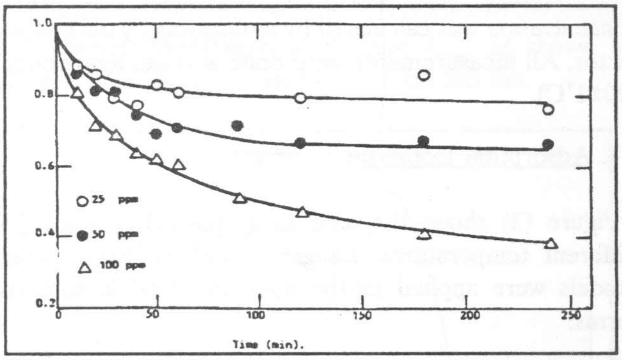

Figure 7. Effect of Initial Concentration, T=20°C, Adsorbent Mass = 1.7g, size = 500-710 μm, speed = 400 rpm.

Figure (6) is a representation for the effect of initial dye concentration on the absorption of the basic dye on adsorbent particles. Experimental data are mentioned on the diagram. The maximum adsorption slightly exceeded 60% of the original dye concentration.

ii. Particle size

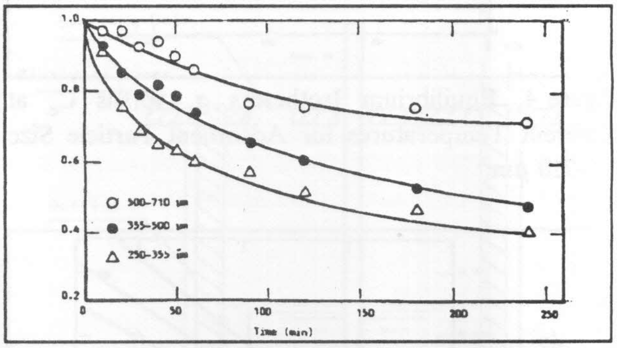

Figure 8. Effect of Particle Size, T=20°C, Adsorbent Mass = 0.425g, C_0 = 100 ppm, speed = 400 rpm.

As shown in Figure (7), the smaller the size of adsorbent particles used, the higher the adsorbed percentage adsorbate. A maximum value attained of about 60% may be considered as acceptable.

iii. Agitation rate

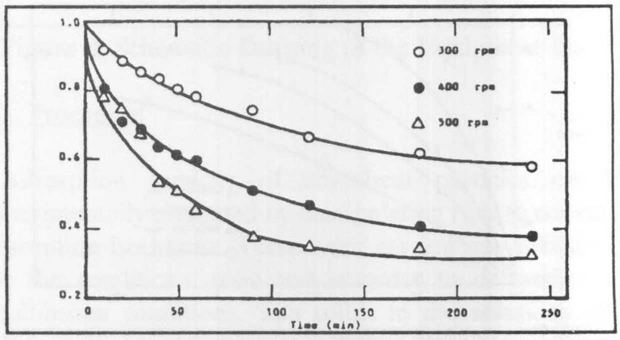

Figure 9. Effect of Impeller Speed, T=20°C, C_0 = 100 ppm, Adsorbent Mass = 1.7g, Size 500-710 μm.

The efficiency of batch agitation, on other hand, was found to be of higher influence on the adsorption capacity; about 80% adsorbance for the dye was attained with as high agitation speed as 500 rpm (Figure (8)).

iv. Adsorbent mass

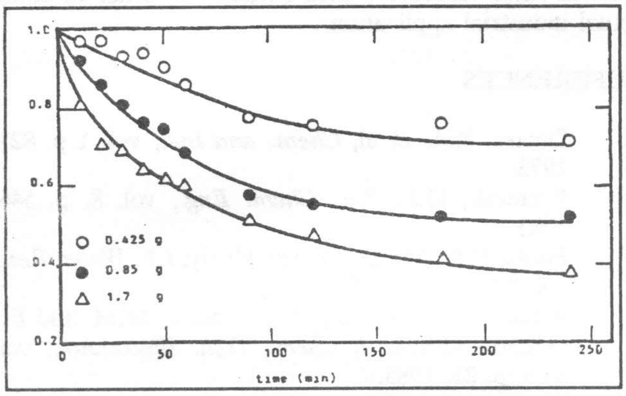

Figure 10. Effect of Adsorbent Mass, T=20°C, C_0 = 100 ppm, size 500-710 μm, speed = 400 rpm.

On Figure (9), the effect of using different adsorbent masses having the same particle size range, under similar agitation condition and with same initial concentration of the dye, had been studied by representing the dimensionless ratio C/C_0 against time of adsorption. As shown, about 60% of the dye had been adsorbed on the adsorbent surfaces in the bath when using 1.7 grams adsorbent in constant bath volume of 1.7 liters.

v. Temperature

No other evidence for the effect of temperature on the adsorption behavior is required, since it is clear from the equilibrium isotherms at different temperatures (Figures (4), (5)) that the curves had leveled at higher q_e values for higher temperatures, which means higher adsorption capacity with increasing temperature of the bath.

6. Heat of Adsorption

To ensure the ease with which adsorption take place on cellulosic agricultural residues, trials had been made to evaluate the heat of adsorption. This was done by following the procedure carried by El-Geundi [5] where K is plotted versus 1/T. A straight line of slope -H/R will result. The heat of adsorption was found to have an approximate value of 4300 J/ mole.

DISCUSSION

It is not surprising that none of the parameters studied within the preceding pages had proved inverse proportionality to the capacity of adsorption of basic dyes on agricultural waste surfaces, lest the reverse will become surprising. Thus, it is well known that higher temperatures of the dye bath means higher activities for mobile ions and thus higher rates of contact between these ions and the adsorbing surfaces; so at higher temperatures of the dye bath it is expected to attain higher total adsorption capacity through higher rates of adsorption also (Figure (3)).

As the initial dye concentration increases in the adsorption bath, the concentration gradient between the bulk of solution and adsorbent surfaces will increase, increasing the migration rate and the final adsorption capacity as well (Figure (6)).

For a fixed volume of adsorbate solution, any increase in the mass of adsorbent will increase the availability of new surfaces for adsorption. The same effect is attained decreasing the particle size of adsorbent for a given mass. Thus higher final adsorption values are expected (Figures (7), (9)).

Mass transfer from the bulk of a solution in a vessel containing solids, is also expected to be effected by the driving force originating from the concentration differences between the solution bulk and the surfaces of solid particles. Migration rates are expected to be suppressed by different resistances including those boundary layers around the solid particle surfaces. In stagnant baths it is thus expected that the effect of these boundary layers to be much more higher than the case if these boundary layers are decreased in thickness and/or become in unstablized conditions. Thus, it is expected that any turbulence in these layers, or their removal as far as it may be possible, will facilitate the accessibility of adsorbate molecules from the bulk of the solution to the adsorbent surfaces. Since agitation is one of the means for attaining these conditions, it is expected that increasing agitation rates (speeds) will deteriorate much more the boundary layers around particles and thus enhancing adsorption rates; as shown on Figure (8).

Thus, another time, the results attained are surprising but on the contrary, they are expected. A subject of importance then is to qualify and quantify these results as related to other results obtained in similar baths of adsorption using traditional adsorbents, the most important of which is the activated carbon.

Some recent publications concerning basic dyes using activated carbon as adsorbent had qualified and quantified the adsorption process [12,13]. The results had proved that basic dyes differ in their capability to be adsorbed on carbon surfaces in liquid media. Basic Red 2 (Saffranine

Red) has a maximum adsorption mass of 390 mg per grm activated carbon while Basic yellow 2 (Deorlene Yellow) has a corresponding value of 1240 mg/g-adsorbent. Under the same conditions of adsorption, basic blue 69 (Astrazone blue) has a maximum adsorption capacity of 900 mg/g-activated carbon. Thus, comparing the adsorption of Basic Blue 69 (Astrazone) in the present investigation, which is of maximum value of about 70 mg/g-residue at 20°C, about 85 mg/g-residue at 30°C and which may attain 95 mg.g-residue as shown in Figure (4), with its adsorption on carbon, one can conclude that the adsorption on agricultural residue has values comparable with those of activated carbon by considering the cost of each of them per unit mass which is about £8/ton and ⇳250/ton for each respectively.

It is also to be noted that the activity of carbon surface towards basic dyes depends on the forces of attraction between them which depend to a large extent on the pH value of the adsorption solution itself as well as on the operational conditions. On the other hand when considering agricultural residues as adsorbents, it should be taken into consideration that due to the cellulosic nature of these residues [14], they attain a negative charge on their surfaces in aqueous solutions [15]. Thus it is expected that cationic dyes (basic dyes), which has their chromosphere ion positively charged, will be attracted preferentially to the negatively charged cellulosic surfaces.

Thus in solution containing basic dyes it is expected that their ions will be adsorbed on the agricultural solid surfaces irrespective of the solution conditions; this adds merits to the use of these adsorbents for basic dyes adsorbates.

The use of olive seeds expression residues will encourage the use of other cellulosic agricultural materials for removal of basic dyes from effluents especially if they are abundant and of disposal characteristics i.e. if their price is very low compared with other adsorbents traditionally used.

CONCLUSION

Cellulosic agricultural residues and wastes may be used as adsorbents for colour removal from industrial effluents, especially those of basic character. These residues are of very low prices compared with those traditional materials usually used as adsorbents such as activated carbon, alumina and silica gel. For efficient use of such residues, their particle sizes, mass per unit volume of liquid effluent and intimate mixing with the effluents considered must be efficiently designed so as to attain the highest possible efficiency for color removal.

It is recommended thus that an economical study must follow, so as to attain accurate statistics about the effective use of agricultural wastes and residues not only for olive seeds expression residues but also for all other accessible agricultural materials in different countries.

The adsorption efficiency of such wastes is considered comparable to those of traditional adsorbents if economical aspect are effectively studied in comparison with its colour removal efficiency.

It is also of interest to test actual industrial effluents for their colour removal using these residues in order to confirm these laboratory data obtained in order to attain actual industrial applications.

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