# SORPTION - DESORPTION ISOTHERMS OF DYES FROM AQUEOUS SOLUTIONS AND WASTEWATERS WITH DIFFERENT SORBENT MATERIALS

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## ABSTRACT

The ability of activated carbon and different low-cost by-products and waste material as sorbents to remove various reactive dyes from aqueous solutions and wastewaters was investigated. All aqueous dye solutions contained 2,000 mg $l^{-1}$ NaCl, to mimic real dye wastewater. Batch kinetic and isotherm experiments were conducted to determine the sorption-desorption behavior of the examined dyes from aqueous solutions and wastewaters by different sorbents, including activated carbon, fly ash, bentonite and bleaching earth.

The results from the aqueous solutions indicate that the form of the isotherm equation is not necessarily unique for best description of both sorption and desorption data. The values of the isotherm parameters are not the same, indicating a significant hysteresis effect.

Of the 9 sorption systems tested, 5 are best described by the Freundlich, 3 by the Langmuir and 1 by the linear sorption model. Of the 7 desorption systems tested, 5 are best described by the Freundlich and 2 by the linear model. In all cases, the sorption capacity for dye removal was higher for activated carbon, followed by fly-ash and then by bentonite.

## INTRODUCTION

Wastewaters from dying and finishing operations in the textile industry are generally high in both color and organic content. Color removal from textile effluents has been the target of great attention in the last few years, not only because of its potential toxicity, but mainly due to its visibility problems (Yu-Li and Thomas, 1995; Morais *et al.*, 1999). Recent estimates indicate that approximately 12% of synthetic textile dyes used each year are lost during manufacture and processing operations and 20% of these lost dyes enter the environment through effluents that result from the treatment of industrial wastewaters (Hwang and Chen, 1993; Nawar and Doma, 1989)

Some existing technologies (oxidative destruction

via UV/ozone treatment, photocatalytic degradation, electrochemical reduction etc.) may have a certain efficiency in the removal of dyes, but their initial and operational costs are so great, that they constitute an inhibition to dying and finishing industries (Kang *et al.* 2000; Churchley, 1998; Ogutveren and Koparal, 1994). On the other hand, low cost technologies do not allow a desired degree of color removal or have certain disadvantages. Therefore, in order to achieve the desired degree of treatment, it is necessary to integrate biological, chemical and physical processes.

Sorption has evolved into one of the most effective physical processes for decolorization of textile wastewaters. The most commonly used adsorbent for color removal is activated carbon, because of its capability for efficiently adsorbing a broad range of different types of adsorbates. However, its use is limited, because of its high cost. Several researchers have been studying the use of alternative materials, which, although less efficient, involve lower costs. Among the studied alternative materials are agricultural, forest, animal and several low-cost industrial by-products such as peat, wood, tree barks, chitin, silica gel, bauxite, bentonite clay, certain synthetic polymeric adsorbents, etc. (McKay *et al.* 1985; Fytianos *et al.*, 1985; Allen *et al.* 1989; Poots *et al.* 1976; Elgeundi 1991).

The objective of this work was to determine and compare the efficiency of removal of color, due to three different dyes from aqueous solutions and wastewaters using different kinds of adsorbents.

## MATERIALS AND METHODS
### Materials
The four different sorbents used in this investigation included powdered activated carbon (Acticarbone S, Ceca, Paris, France) and the three low-cost or waste materials, namely: Bentonite (Clarvin, Gador, Spain) bleaching earth (Tonsil 414 FF, Sud-Chemie, AG, Munchen, Germany) and fly ash. Fly ash was collected from the thermal power plant located in Ptolemais, Northern Greece. Based on manufacturers' data, the BET surface areas of activated carbon and bleaching earth were 1,000 $m^2g^{-1}$ and bleaching earth were 1000 $m^2g^{-1}$ and 200 $m^2g^{-1}$ respectively. Fly ash surface area ranged between 0.75-0.8 $m^2g^{-1}$ (Papachristou,1982). All adsorbents were dried at 100°C for 24h before use. Three dyes were studied, namely dye 1, Cibacron Blau F-R (C.I. 182), dye 2, Reactive Blue 21 (C.I. 21) and dye 3, Cibacron Rot F-B (C.I. 184). Real dye wastewater was received from a textile finishing plant, right after the biological treatment stage.

### Methods
The effect of contact time and sorbent dosage on color removal was studied in a series of kinetic and equilibrium experiments. The experimental conditions were deliberately chosen to mimic conditions of dye wastewaters. Therefore, all artificial dye wastewaters contained 2,000 mg $l^{-1}$ NaCl.

### Kinetic Experiments
In each kinetic experiment, a known quantity of sorbent was contacted with a dye solution in a 250 ml flask and was shaken at room temperature for a given recorded time (0.15, 0.30, 0.50, 1, 2, 3, 4, 5, 24, 48, 72 h). The initial concentrations of sorbents (g $l^{-1}$) and dyes (mg $l^{-1}$) are presented in Table 1. The contents of each flask were then allowed to settle, followed by vacuum filtration through 0.45 µm Whatman microfiber filters. The

*Table 1.* Initial concentrations of dyes (mg $l^{-1}$) and sorbents (g $l^{-1}$) used in the sorption kinetic experiments

| Sorbent | Dye 1 | Dye 2 | Dye 3 |
|---|---|---|---|
| | Sorbent | Sorbent | Sorbent |
| Bleaching Earth | 50 mg $l^{-1}$ | 50 mg $l^{-1}$ | 50 mg $l^{-1}$ |
| | 0.15 g $l^{-1}$ | 0.15 g $l^{-1}$ | 0.15 g $l^{-1}$ |
| Activated carbon | 50 mg $l^{-1}$ | 50 mg $l^{-1}$ | 50 mg $l^{-1}$ |
| | 0.6 g $l^{-1}$ | 0.6 g $l^{-1}$ | 0.6 g $l^{-1}$ |
| Fly Ash | 50 mg $l^{-1}$ | 50 mg $l^{-1}$ | 50 mg $l^{-1}$ |
| | 1 g $l^{-1}$ | 1 g $l^{-1}$ | 1 g $l^{-1}$ |
| Bentonite | 50 mg $l^{-1}$ | 50 mg $l^{-1}$ | 50 mg $l^{-1}$ |
| | 0.5 g $l^{-1}$ | 0.5 g $l^{-1}$ | 0.5 g $l^{-1}$ |

amount of dyes sorbed was determined by difference between the initial and final concentrations measured spectrophotometrically with a Hitachi U-2000 spectrophotometer. These experiments were used to establish the equilibrium time between the sorbents and the dye solutions. This equilibrium time was used as contact time in the isotherm experiments.

## Equilibrium Experiments

In the sorption isotherm experiments dye solutions were added to different quantities of sorbents into glass-stoppered bottles and subsequently placed on a shaker for 72h at 20°C. The initial concentrations of sorbents (g l$^{-1}$) and dyes (mg l$^{-1}$) in the sorption flasks are presented in Table 2. The amounts sorbed were determined by difference between initial an final concentrations and expressed as mg of dye/g of sorbent. In each case, duplicate blank experiments were also conducted. For desoprtion isotherm experiments, the remainder of the supernatant of the sorption flasks after settling was removed and 100 ml of a 2,000 mg l$^{-1}$ NaCl solution were added to the sorbent residue in each flask. The mixture was allowed to equilibrate for 72 hours on a shaker and was centrifuged at 4,000 rpm for 15 min. The concentration of the dyes desorbed was determined, in the supernatant.

Similar procedures were followed for experiments with real wastewaters.

## RESULTS AND DISCUSSION
### Kinetic experiments with aqueous dye solutions

Percent removal of the examined dyes by the different sorbents, as a function of contact time, are shown in Fig. 1. Under the conditions of the experiments all systems approached equilibrium within 72 h of contact time.
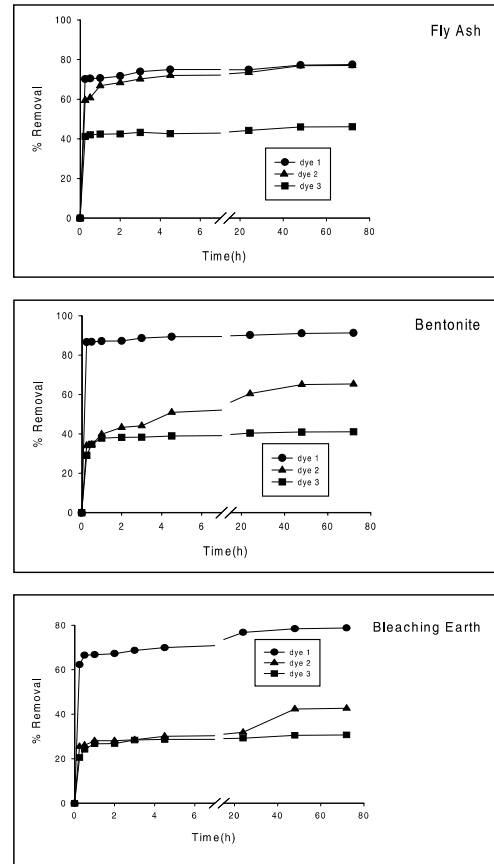


*Figure 1.* Kinetics of dye removal by the examined sorbent materials

## Sorption isotherm experiments with aqueous dye solutions

It is generally possible to express the results of experimental sorption measurements in the form of equilibrium sorption isotherms. In this study, three types of isotherms have been investigated, namely the linear, the Langmuir and Freundlich isotherm (Choi and Cho, 1996). The sorption process is then discussed in terms of constants, which are character-

*Table 2.* Initial concentrations of dyes (mg l$^{-1}$) and sorbents (g l$^{-1}$) used in the sorption isotherm experiments

| Sorbent | Dye 1 | Dye 2 | Dye 3 |
|---|---|---|---|
| | Sorbent | Sorbent | Sorbent |
| Bleaching Earth | 5–100 mg l$^{-1}$ / 0.15 g l$^{-1}$ | 5–100 mg l$^{-1}$ / 0.15 g l$^{-1}$ | 5–100 mg l$^{-1}$ / 0.15 g l$^{-1}$ |
| Fly Ash | 5–100 mg l$^{-1}$ / 0.6 g l$^{-1}$ | 5–100 mg l$^{-1}$ / 0.6 g l$^{-1}$ | 5–100 mg l$^{-1}$ / 0.6 g l$^{-1}$ |
| Bentonite | 5–100 mg l$^{-1}$ / 1.0 g l$^{-1}$ | 5–100 mg l$^{-1}$ / 1.0 g l$^{-1}$ | 5–100 mg l$^{-1}$ / 1.0 g l$^{-1}$ |

*Table 3.* Goodness of fit of the linear, Freundlich and Langmuir isotherms to the sorption experimental data. Values corresponding to best fit isotherms are shown in bold

| Absorbents | $R^2$ values | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Linear isotherm | | | Freundlich isotherm | | | Langmuir isotherm | | |
| | dye 1 | dye 2 | dye 3 | dye 1 | dye 2 | dye 3 | dye 1 | dye 2 | dye 3 |
| Activated Carbon | 0.518 | 0.468 | 0.622 | **0.983** | 0.969 | 0.961 | 0.984 | **0.974** | **0.988** |
| Fly ash | 0.724 | 0.235 | 0.814 | **0.967** | 0.901 | **0.876** | 0.933 | **0.981** | 0.841 |
| Bentonite | 0.871 | **0.892** | 0.975 | **0.916** | 0.860 | **0.997** | 0.868 | 0.838 | 0.894 |

istic for the individual systems (Wang *et al.*, 1990; Nassar and Elgeundi, 1991). The linear isotherm indicates a partioning process of the solute onto the sorbent. The Langmuir equation assumes that there is no interaction between the sorbate molecules and that the sorption is localized in a monolayer. It is then assumed that once a dye molecule occupies a site, no further sorption can take place at that site. Theoretically, therefore, a saturation value is reached, beyond which no further sorption can take place. The Freundlich equation is an empirical relationship describing the sorption of solutes from a liquid to a solid surface. The equations for the three types of sorption isotherms are given by:

Linear isotherm $\qquad x/m = K_p C_e$
Langmuir isotherm $\qquad C_e/(x/m) = 1/ab + (1/a)C_e$
Freundlich isotherm $\qquad x/m = KC_e^{1/n}$

where $C_e$ is the equilibrium concentration of dyes in solution (mg l$^{-1}$), x/m is the amount of dye sorbed per unit of sorbent (mg g$^{-1}$), "a" is a constant related to the area occupied by a monolayer of sorbate, reflecting the sorption capacity (mg g$^{-1}$), "b" is a direct measure for the intensity of the sorption process (l mg$^{-1}$), K represents the quantity of dye sorbed in mg g$^{-1}$ adsorbent for a unit equilibrium concentration of the compound under test (i.e. $C_e = 1$) and 1/n is a measure for the sorption intensity. For n=1 the partition between the two phases is independent of the concentration. In this case, $K \equiv K_p$ (Iinear isotherm). A value for 1/n below one indicates a normal Langmuir isotherm, while 1/n above one is indicative for a cooperative sorption (Mohan and Karthikeyan, 1997; Atkins, 1970).

In order to decide which type of isotherm fits better the sorption experimental data, we plotted the quantities x/m vs $C_e$ for the linear isotherm, log (x/m) vs log $C_e$ for the Freundlich isotherm and $C_e/(x/m)$ vs $C_e$ for the Langmuir isotherm. The $R^2$ values (goodness of fit criterion) computed by linear regression for the three types of isotherms are presented in Table 3 for all sorbents.

The data of Table 3 indicate that the best fit isotherm is a function of the sorbent and sorbate considered each time. For example, the Freundlich isotherm is most appropriate for sorption of dye 1 by activated carbon, fly ash and bentonite. The Langmuir isotherm is most appropriate for sorption of dye 2 by activated carbon and fly ash and the linear isotherm is most appropriate for sorption of dye 2 by bentonite. The Langmuir, Freundlich and Freundlich isotherms are best suited for sorption of dye 3 by activated carbon, fly ash and bentonite respectively. The best fit isotherm parameters are summarized in Table 4. Comparison between experimental data and best fit isotherm curves is presented in Figure 2.

### Effect of pH

The solution pH values ranged between 3 and 11. No attempt was made to control the aqueous pH values by buffer addition in the isotherm experiments.

In experiments using activated carbon as sorbent, the % dye removal varied as follows: For dye 1, from 88.9 % at pH 11 to 99.9% at pH 3. For dye 2, from 66.6% at pH 9 to 76.0% at pH 3. For dye 3, from 77.3% at pH 11 to 87.5% at pH 3. Removal of dyes, 1 and 2 by activated carbon was higher at lower pH values. Removal of dye 3 presented a plateau at lower values in the pH range 5-9 (Figure 3).

In experiments using fly ash as sorbent, the % dye removal varied as follows: For dye 1, from 71.2% at pH 7 to 80.9% at pH 3. For dye 2, from 56.3% at pH 9 to 87.8% at pH 11. For dye 3, from 30.5% at pH 7 to 48.9% at pH 3. Removal of dyes 1 and 2 by fly ash was higher at lower pH values. Removal of dye 3 was lower in the pH range 5-7 (Figure 3).

In experiments using bentonite as sorbent, dye removal varied as follows: For dye 1 from 59.3% at pH =11 to 78.9% at pH = 9, for dye 2 from 41.0% at pH = 5 to 47.9% at pH = 9 and for dye 3 from 24.2% at pH = 5 to 32.8% at pH = 3.

*Table 4.*    Best fit isotherm parameters for sorption from aqueous solutions

| Sorbent | Dye 1 | Dye 2 | Dye 3 |
|---|---|---|---|
| Activated Carbon | Freundlich K = 174 ± 8.5 $1/n = 0.513 ± 2.8×10^{-2}$ | Langmuir a = 357 ± 24 b = 0.275 ± 0.16 | Langmuir a = 455 ± 20 b = 0.155 ± 0.021 |
| Fly ash | Freundlich K = 41 ± 2 $1/n = 0.274 ± 2.1×.10^{-2}$ | Langmuir a = 94,3 ± 4,8 b = 0.465 ± 0.42 | Freundlich K = 18.7 ± 1,5 $1/n = 0.237 ± 3.4×10^{-2}$ |
| Bentonite | Freundlich K = 15.4 ± 1.9 $1/n = 0.390 ± 4.5×10^{-2}$ | Linear $K_p = 0.464 ± 0.11$ | Freundlich K = 0.87 ± 0.07 $1/n = 0.845 ± 1.75×10^{-2}$ |

Units: $K_p$: $\left(\dfrac{1}{g}\right)$, K: $\left(\dfrac{mg}{g}\right)\left(\dfrac{1}{mg}\right)^{1/n}$, a: $\left(\dfrac{mg}{g}\right)$, b: $\left(\dfrac{1}{mg}\right)$
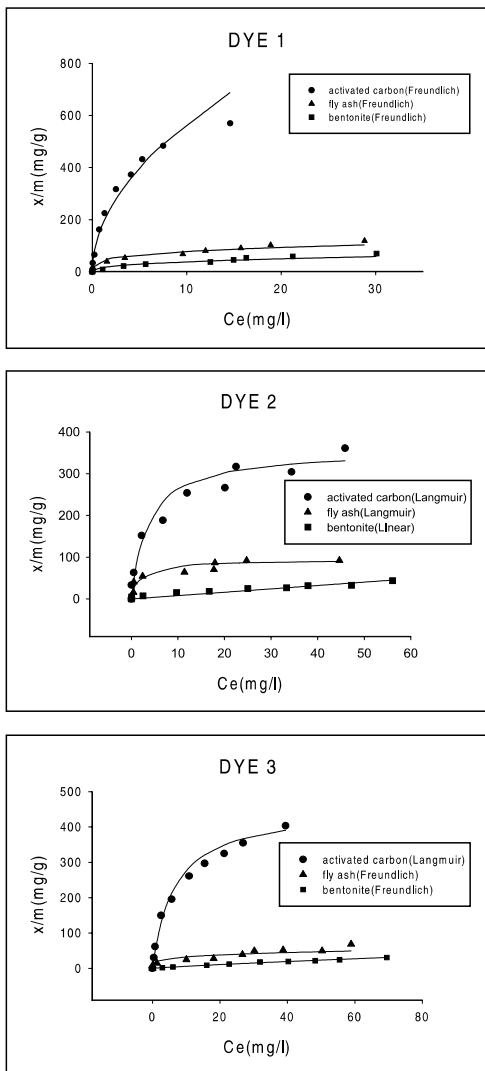


*Figure 2.*    Comparison between experimental data and best fit sorption isotherm curves, based on the parameters of Table 4
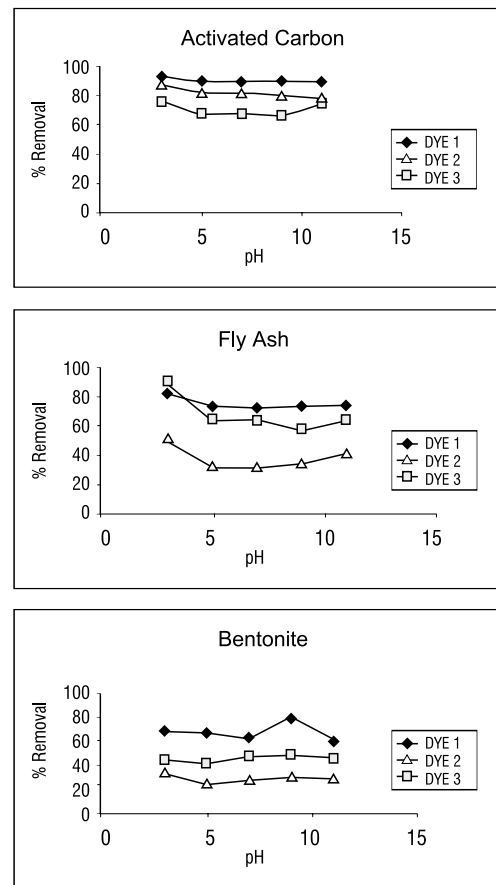


*Figure 3.*    Effect of pH on *% removal* of dyes from aqueous solutions by the different sorbents

## Desorption isotherm experiments with aqueous solutions

Following a procedure similar to the one used for sorption isotherms, we determined the best fit isotherm model for the desorption experimental

*Table 5.* Goodness of fit of the linear, Freundlich and Langmuir isotherms to the desorption experimental
data. Values corresponding to the best fit isotherms are shown in bold

| Absorbents | $R^2$ values | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Linear isotherm | | | Freundlich isotherm | | | Langmuir isotherm | | |
| | dye 1 | dye 2 | dye 3 | dye 1 | dye 2 | dye 3 | dye 1 | dye 2 | dye 3 |
| Activated Carbon | 0.766 | **0.948** | **0.856** | **0.926** | 0.908 | 0.761 | 0.922 | 0.638 | 0.278 |
| Fly ash | 0.887 | 0.928 | 0.897 | **0.939** | **0.959** | **0.962** | 0.773 | 0.785 | 0.681 |
| Bentonite | - | - | 0.773 | - | - | **0.949** | - | - | 0.641 |

*Table 6.* Best fit isotherm parameters for desorption from aqueous solutions

| Sorbent | Dye 1 | Dye 2 | Dye 3 |
|---|---|---|---|
| Activated Carbon | Freundlich<br>K = 454 ± 0.12<br>1/n=0.624± 4.8×10$^{-4}$ | Linear<br>K$^p$ = 207 ± 20 | Linear<br>K$_p$ = 186 ± 29 |
| Fly ash | Freundlich<br>K = 32.8 ± 3.2<br>1/n = 0.610±6.9×10$^{-2}$ | Freundlich<br>K = 28.1 ± 2,0<br>1/n = 0.411±3.5.10$^{-2}$ | Freundlich<br>K = 4.1 ± 0.639<br>1/n = 1.42 ± 1.1 .10$^{-1}$ |
| Bentonite | Not determined | Not determined | Freundlich<br>K = 22.7 ± 2.394<br>1/n = 3.05 ± 2.67 ± 10$^{-1}$ |

Units: $K_p$: $\left(\dfrac{1}{g}\right)$, K: $\left(\dfrac{mg}{g}\right)\left(\dfrac{1}{mg}\right)^{1/n}$, a: $\left(\dfrac{mg}{g}\right)$, b: $\left(\dfrac{1}{mg}\right)$

data. The $R^2$ values (goodness of fit criteria) computed by linear regression for the 3 types of isotherms are presented in Table 5 for all sorbents. The best fit isotherm parameters selected on the basis of Table 5 are presented in Table 6. Figure 4 presents a comparison between experimental data and best fit isotherm curves, based on the parameters of Table 6.

Comparison between Tables 4 and 6 reveals the following:

1. The form of the isotherm equation is not necessarily unique for best description of both sorption and desorption data. For example, the Langmuir isotherm is the most appropriate for describing sorption data for dye 2 by fly ash, whereas the Freundlich isotherm is the most appropriate for describing the respective desorption data.

2. The Freundlich model is the best-fit isotherm in 5 of the 9 sorption systems tested and in 5 of the 7 desorption systems tested. The Langmuir model is the best fit isotherm in 3 of the 9 sorption systems tested and in non of the

7 desorption systems tested. The linear models is the best fit isotherm in one of the 9 sorption systems tested and in 2 of the 7 desorption systems tested.

3. Comparison of Tables 4 and 6 indicates that the values of the isotherm parameters are not the same, indicating a significant hysteresis effect.

## Treatment of dye wastewater

Dye wastewater from a textile plant was obtained and characterized in terms of the parameters pH, COD, BOD and absorption at 550 nm (Table 7).

*Table 7.* Dye wastewater characterization

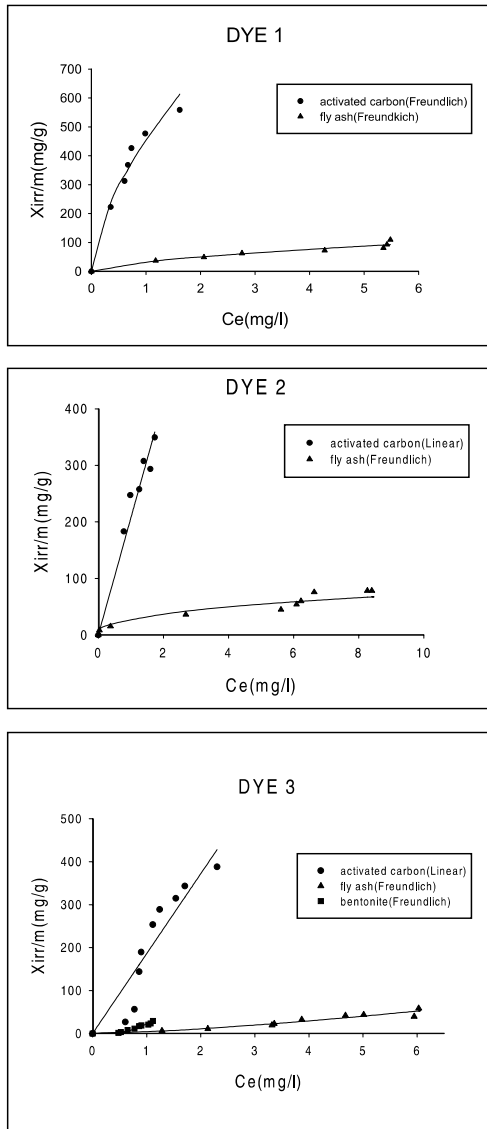| Parameter | Value |
|---|---|
| pH | 7.5 |
| BOD$_5$ (mg l$^{-1}$) | 214 |
| COD (mg l$^{-1}$) | 230 |
| DO (mg l$^{-1}$) | 2.4 |
| Absorption at 550 nm | 2.224 |

*Figure 4.* Comparison between experimental data and best fit desorption isotherm curves, based on the parameters of Table 6



Figure 5. Kinetics of removal of wastewater constituents absorbing at 550 nm by the examined sorbent materials

As in the case of single dye experiments, kinetic experiments were conducted first, in order to determine the required contact time for equilibrium experiments. The experimental results of the kinetic experiments are presented in Figure 5, in terms of % removal vs contact time. The removal refers to wastewater constituents absorbing at 550 nm and was computed using the equation:

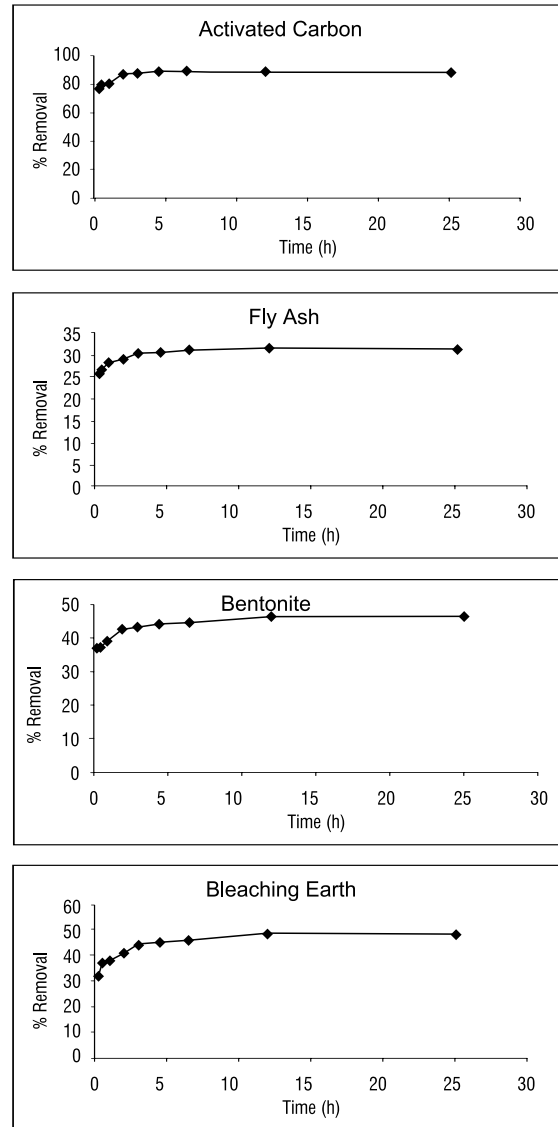$$\% \text{ Removal} = \frac{\text{Abs}_o - \text{Abs}_t}{\text{Abs}_o}$$

According to Figure 5, the equilibrium time determined for all sorbents was 24 hours.
Equilibrium experiments were conducted, using varying amounts of sorbent in the same volume of wastewater, at 24 hours contact time. The sorption equilibrium results are presented in Figure 6. In the case of activated carbon, high removals were observed at relatively low sorbent doses, i.e., 90% at 500 mg $l^{-1}$ dose of activated carbon. In the case of fly ash, bentonite and bleaching earth, removals are much lower compared to those observed for activated carbon.
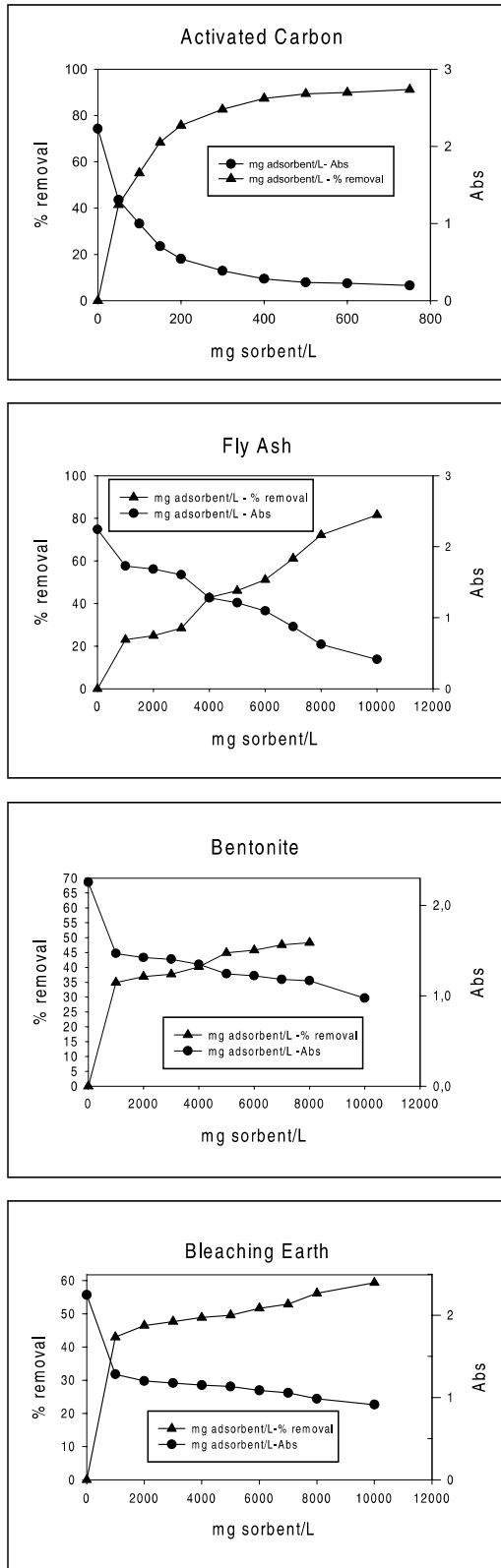
Figure 5.   Kinetics of removal of wastewater constituents absorbing at 550 nm by the examined sorbent materials

Thus, at the same dose (500 mg $l^{-1}$) the % removal of fly ash, bentonite and bleaching earth are 15.5, 32.9 and 42.8%, respectively. The choice of the appropriate sorbent is not only matter of sorption capacity, but also regeneration, waste management, and total cost of treatment. Taking these into account, it may turn out that a cheap sorbent with low sorption capacity is more appropriate than the expensive activated carbon under some waste-specific circumstances.

## CONCLUSIONS

The removal of color from aqueous solutions and wastewaters using activated carbon and three low cost sorbent materials (bentonite, fly ash, bleaching earth) was studied.

Kinetic experiments were conducted in order to determine the equilibrium contact time and use it in the isotherm experiments. This time was found to be 72 h in the case of the aqueous solutions of dyes and 24h in the case of the wastewaters used.

Three types of isotherms were investigated, namely the linear, Langmuir and Freundlich isotherms. The form of isotherm equation which best describes the sorption and desorption of dyes was determined according to the $R^2$ values, known as goodness of fit criterion. It was concluded that the form of the isotherm equation is not necessarily unique for best description of both sorption and desorption data. The Freundlich model was the best fit isotherm in 5 of the 9 sorption systems tested and in 5 of the 7 desorption systems tested. The Langmuir model was the best fit isotherm in 3 of the 9 sorption and in none of the 7 desorption systems tested. The Linear model was the best fit isotherm in one of the 9 sorption and in 2 of the 7 desorption systems tested. The values of the isotherm parameters between sorption and desorption are not the same, indicating a significant hysteresis effect.

Sorption was an effective process for decolorization of textile wastewaters. Although activated carbon was the most effective sorbent, other low cost sorbents could be used for color removal. The final choice of the sorbent is a matter of economics.

## REFERENCES

Allen, S., Khader, K. and McKay, G. (1989), Equilibrium adsorption-isotherms for basic dyes onto lignite, *J. Chem. Tech. Biotechnol.* **45**, 291-302.

Atkins P. (1970), Physical Chemistry, Oxford University Press, Oxford UK.

Choi, Y and Cho, J. (1996), Color removal from dye waste water using vermiculite. *Environ. Technol.* **17**, 1169-1180.

Churcley, J. (1998), Ozone for dye waste color removal, *Ozone-science and Engineering*, **20**, 111-120.

El Geundi M. (1991), Color removal from textile effluents by adsorption techniques, *Wat. Res.* **25**, 271-275.

Fytianos K., Vasilikiotis G., Agelidis T., Kofos, P. and Stefanidis, K. (1985) Color removal from dye containing effluents by treatment with manganese solid waste, *Chemosphere*, **14**, 411-416.

Hwang, M. and Chen, K. (1993), Removal of color from effluents using polyamide-epichlorohydrin-cellulose polymer II. Use in acid dye removal, *J of Applied Polymer Science*, **49**, 975-989.

Kang S., Liao C. and Po, S. (2000), Decolorization of textile wastewater by photo-fenton oxidation technology, *Chemosphere*, **41**, 1287-1294.

McKay, G., Otterburn, M. and Aga, J. (1985), Fuller's earth and fired clay as adsorbents for dye stuffs equilibrium and rate studies, *Water, Air and Soil Pollution*, **24**, 307-312.

Mohan, S. and Karthikeyan, J. (1997), Removal of lignin and tannin color from aqueous solution by adsorption onto activated charcoal, *Environ. Pollut.* **97**, 183-187.

Morais, L., Freitas O., Gancolves E., Vaskancelos, L. and Gonzalez, C. (1999), Reactive dyes removal from wastewaters by adsorption on eucalyptus bark: Variables that define the process, *Wat. Res.* **33**, 979-988.

Nassar, M. and Elgeundi, M. (1991), Comparative cost of color removal from textile effluents using natural adsorbents, *J. Chem. Tech. Biotechnol.* **50**, 257-264.

Nawar, S. and Doma, H. (1989), Removal of dyes from effluents using low-cost agricultural by-products, *Sci. Tot. Environ.* **79**, 271-279.

Ogutveren, U. and Kaparal, S. (1994), Color removal from textile effluents by electrochemical destruction, *J. Environ. Sci. Health*, **A 29**, 1-16.

Papachristou-Kolovea, E. (1982), The use of fly ash for lead removal from industrial wastes, PhD Dissertation, Aristotle University of Thessaloniki, 76-79.

Poots, V., McKay, G. and Healy, J. (1976), The removal of acid dye from effluent using natural adsorbents, *Wat. Res.* **10**, 1067-1074.

Wang, H., Huang, D. and Yao, W. (1990), Study on mechanisms of adsorption and competition among sensitizing dyes, *J. of Imaging Science*, **34**, 182-186.

Yu-Li Yeh, R. and Thomas, A. (1995), Color difference Measurement and color removal from dye wastewaters using different adsorbents, *J Chem Tech Biotechnol*, **63**, 55-59.