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Adsorption of Anionic Reactive Dyes from Solution by Activated Carbon: Effect of Solution pH

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The influence of pH on reactive dyes adsorption from solution is studied in this paper. The adsorbent used was filtrasorb 400 (FS-400) which showed a high equilibrium capacity for hardly adsorbable reactive dyes. The adsorption performance of FS-400 was not affected over a wide pH range (3–10), hence FS-400 is considered as a pH-insensitive adsorbent. Hydrolysed reactive dyes, the state at which reactive dyes are usually discharged, were effectively adsorbed by FS-400. Capacities ranging from 20–80% by weight of FS-400 have been realized.

Key Words: Adsorption, pH, Reactive dyes, pH-Insensitive adsorbents, Activated carbon.

INTRODUCTION

The effectiveness of commercial activated carbons for removing reactive dyes has been reported[1]. The effect of carbon type and intrinsic chemical properties of carbons on dyes adsorption has also been investigated by the authors[2]. On weight basis, it was found that activated carbon adsorbs reactive dyes from 20 to 70% of its weight. Because of the ease of preparation from many natural sources activated carbon could be considered as abundant adsorbent for reactive dyes[2]. Reactive dyes have a poor adsorbability on wide range of adsorbents[1–3]. In fact, the occurrence of negatively charged group like sulfonate group (Fig. 1) retards adsorption of reactive dyes[4]. Solution pH is probably the most important parameter related to the adsorption from solution. Solution pH has little effect on organic adsorption while it has a dominant effect on metal adsorption due to hydrolysis by hydroxide ions. Because H^+ and OH^- ions are adsorbed quite strongly, so the adsorption of other species (dyes in this work) are supposed to be affected by the pH of solution. pH affects adsorption in that it governs the degree of ionisation. Therefore, for any practical investigation it is worthwhile to investigate the effect of solution pH on adsorbent capacity. Adsorbents which work over a wide pH range, *i.e.*, pH-insensitive, are recommended over pH-sensitive adsorbents. It is important to study the adsorbability of hydrolysed reactive dyes as they discharge in that state[5]. In this work the effect of dye solution pH

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on adsorption capacity will be examined over a wide pH range (2–12). The effect of hydrolysis of reactive dyes by Na_2CO_3 on adsorption will be investigated.

EXPERIMENTAL

Adsorbent and Adsorbate: The commercial activated carbon used in this research is Filtrasorb 400 (FS-400). FS-400 was selected due to its high adsorption in solution. Physical and chemical properties of FS-400 are shown in Table-1. Samples of FS-400 were sieved using a standard British Sieves apparatus (Endecotts Ltd., London, England). Adsorptive capacities at different pH were evaluated in the size range 600–710 μm. The adsorbent was used as received without any further treatment. To eliminate the effect of long storage times, *i.e.*, to minimize the oxidation of carbon surfaces with air, the adsorbent was kept in dry sealed glass bottles.

TABLE-1
CHARACTERISTICS OF FS-400 ACTIVATED CARBON*

Origin	Method of preparation	Surface area ($m^2 g^{-1}$)	Bulk density ($g cm^{-3}$)	Iodine value ($mg g^{-1}$)	Carbon type**
Bituminous Coal	Physically	1100	0.43	1050	H

*FS-400 carbon supplied from Chemviron Carbon, UK.
†H-carbons are those carbons which have alkaline suspension[1].

Reactive dyes, adsorbates used herein represent about 20–30% of the dyes used worldwide. Their usage has increased by approximately 15% per year since 1980[1–3]. They are characterized by nitrogen to nitrogen double bond (N═N), azo bond. Three reactive dyes were studied; namely, Remazol Reactive Yellow (monoazo group, one N═N bound), remazol reactive black (diazo group, two N═N bonds) and remazol reactive red (diazo group, two N═N bonds) (Bayer, Frankfurt, Germany). The studied dyes were soluble in water (generally as all reactive dyes) and showed a moderate pH (4.5–5) in distilled water at 1000 ppm concentration. Generally, chemical structures of commercial reactive dyes were not provided due to commercial reasons. The chemical structure of remazol reactive black was disclosed by the manufacturer for the purpose of research, which is shown in Fig. 1.

TABLE-2
λ_{max} FOR MAXIMUM ABSORBANCE OF DYES

Dye Name	λ_{max} (nm)	Dye type
Reactive Yellow	410	Anionic
Reactive Red	520	Anionic
Reactive Black	597	Anionic

Effect of Solution pH on Carbon Capacity

Wide pH range was selected to represent highly acidic, acidic, neutral, alkaline and highly alkaline conditions. As most reactive dyes were discharged in their hydrolysed states, so it is important to carry out adsorption studies at that chemical state to obtain realistic results for adsorption from solution. Hydrolysed dyes were prepared by adding Na_2CO_3 powder[5, 6]. Dye solution pH was raised to 11.50 after hydrolysis for all systems. The aqueous adsorption capacity of FS-400 at different pH values was studied using single-point adsorption tests. These tests are not intended to determine adsorption capacity but to illustrate the effect of solution pH on reactive dyes adsorption. A similar procedure was used by Miguel and co-workers[7]: 0.050 g of FS-400 at 600–710 μm particle diameter was added to 50 mL dye solution and agitated at 25 ± 1°C for three weeks to ensure equilibrium. pH of dye solution was determined before carbon addition. During pH adjustment, readings were taken after 2 min of stirring. A digital pH meter was used for that purpose (WPA Linton, England). Nitric acid and sodium hydroxide were used to obtain different pH values. All reagents used were of analytical reagent grade. For each pH value, the equilibrium concentration was compared to a blank solution which has the same pH value. This procedure was adopted to reduce any deviations in dye measurements which may occur at different pH conditions. Carbon removal capacity (%) was calculated from the difference between samples taken and blanks concentration according to the following mass balance equation:

$$\text{Adsorption Yield (\%)} = (C_0 - C_e/C_0) \times 100 \qquad (1)$$

where C_0 and C_e are the concentrations (mg dm^{-3}) of dye in the initial and equilibrated solutions, respectively.

RESULTS AND DISCUSSION

Effect of pH on reactive dyes adsorption

As mentioned earlier, pH of adsorbate solution has a considerable effect on adsorption magnitude. This effect is usually higher in the case of metal adsorbates as pH of medium determines the extent of hydrolysis of metal cations. Adsorption magnitude of reactive dyes may be affected as a result of occupation of active sites on carbon surface with highly adsorbable H^+ and OH^- ions.

Before commencing discussion of the results, it is worthy of mention that pH of dye solution has a high influence on the chemical characteristics of activated carbon. Therefore, FS-400 at solution $pH > 7.1$ will have a basic chemical characteristic, while at $pH < 7.1$ the adsorbent will acquire an acidic characteristic. At $pH = 7.1$ the surface charge is zero and this pH is called zero point of charge, pH_{zpc}[8]. Based on laboratory observation, reactive dyes (at 1000 mg dm^{-3}) start to hydrolyse after $pH = 10$. Undoubtedly, these facts will help when discussing the variations in dyes adsorption with varying pH of solution. Effect of solution pH on adsorption of reactive dyes is depicted in Fig. 2.

As could be seen in Fig. 2, reactive yellow has a higher capacity for FS-400 comparing to other two dyes. As dyes were treated by the same adsorbent, so the differences in their adsorption capacities were mainly attributed to the differences in corresponding chemical characteristics. In fact, it is a hard task to explain the differences in dyes adsorption capacities as only one of the structures is disclosed, reactive black (Fig. 1).

As the lines indicate in Fig. 2, FS-400 capacity has not greatly affected the pH range (3–10). Based on that, it can be inferred that OH^- and H^+ ions do not compete with dyes adsorption in the pH range (3–10). It has been reported that the performance of some type of adsorbents is highly affected by solution pH (*i.e.*, pH sensitive adsorbents)[9]. The high capacity of FS-400 for reactive dyes over a wide pH range, makes FS-400 a suitable adsorbent to purify wastewater which usually has fluctuating pH conditions. In particular, textile wastewater containing reactive dyes has an alkaline condition; hence FS-400 can also be beneficial. As shown in Fig. 2, there is an increase in the removal capacities at pH < 3 and pH > 10 for the three adsorption systems. In general, adsorption of organic pollutants from water onto activated carbon is increased with decreasing pH[10]. In many cases this may result from neutralisation of negative charges at the surface of the carbon with increasing H^+ ion concentration, by reducing hindrance to diffusion and making available more of the active surface of the carbon. As

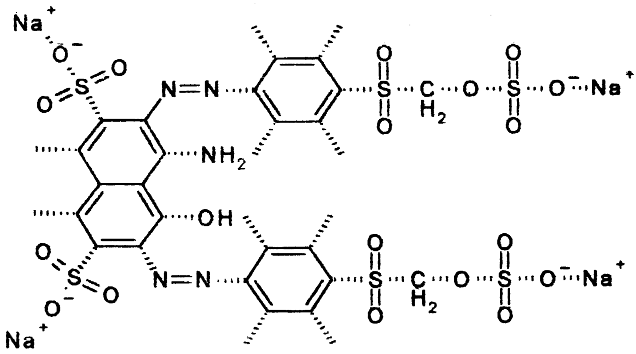

Fig. 1. Chemical structure of Remazol Reactive Black

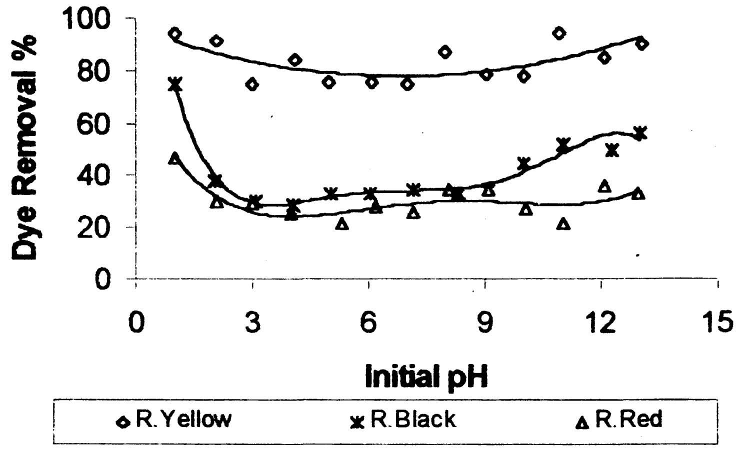

Fig. 2. Effect of solution pH on removal capacity
(Carbon mass = 0.05 g; volume of solution = 0.05 dm^3; dye concentration = 1000 mg dm^{-3})

reactive dyes have anionic nature, so it can be expected to have more attraction at lower pH. In alkaline condition where a high concentration of OH^- is present, the possibility of forming negative surface charge is expected. As dyes at that pH were in a different chemical state (hydrolysed state), so a different mechanism, rather than electrostatic attraction-repulsion, was involved.

Namasivayam and Yamuna[11] showed that the adsorption of anionic dyes decreased from 100 to 65% on increasing pH of solution from 2.7 to 10.2. The authors attributed the increase in adsorption at lower pH to the potential attraction between adsorbent and dye, while at higher pH ($pH > pH_{zpe}$) the sorbent acquires a negative charge which lowers anionic dye adsorption. It seems that such an explanation cannot explain the adsorption behaviour of reactive dyes on FS-400 at higher pH. pH_{zpe} of FS-400 is 7.1, *i.e.*, FS-400 acquires a negative charge at pH higher than 7.1 and accordingly a lower adsorption for reactive dyes is expected. This was not the case herein, where FS-400 capacity was not changed over the pH range 3–10. Indeed, FS-400 is an effective adsorbent which can work in solutions of different pH conditions (Fig. 2). In agreement with our results, Lee and co-workers[12] showed that bleaching earth is capable of taking up negatively charged reactive dyes over a wide pH range.

It seems that adsorption at higher pH is quite complicated and the explanation seems to be complex[13]. In a different study, Karcher and co-workers[14] have studied the effect of pH solution on sorption of Remazol Reactive Black 5, the same dye as examined in this work, on Cucurbituril[14]. The adsorbent was effective in the pH range (2–8). A high increase in adsorption was observed after pH = 8.

Effect of hydrolysis by Na_2CO_3 on dye adsorption

Regarding the effect of dye hydrolysis upon adsorption, equilibrium results showed that FS-400 is an effective adsorbent for both hydrolysed and unhydrolysed reactive dyes, Table-3. We have referred to dyes treated with Na_2CO_3 as hydrolysed dyes.

Unlike the other two dyes, reactive red has a higher adsorption capacity after hydrolysis. The results in Table-3 show that FS-400 can adsorb hydrolysed reactive dyes from 20–80% of carbon weight. The high capacity of FS-400 for hydrolysed reactive dyes widens its applicability for treating real textile wastewater where dyes are in hydrolysed state.

TABLE-3

ADSORPTION CAPACITIES (mg g^{-1}) OF UNHYDROLYSED AND HYDROLYSED REACTIVE DYES

Dye	Adsorption capacity (mg g^{-1}) unhydrolysed dye[1]	Adsorption capacity (mg g^{-1}) hydrolysed dye[2]
Reactive yellow	770	730
Reactive black	333	310
Reactive red	213	320

[1] pH of solution ≈ 5.;5 [2] pH of solution ≈ 11.5

Sorption capacity of different adsorbents for hydrolysed reactive dyes was recently investigated. Natural adsorbents showed a good capacity for removing hydrolysed reactive dyes from solution[5, 6], however, the adsorption capacity of FS-400 reported in this work (Table-3) are higher than those reported in literature[5, 6].

Conclusion

The experimental results prove the high capacity of FS-400 for reactive dyes. In addition, the capacity is not affected over a wide pH range (3–10). Therefore, FS-400 is considered as a pH-insensitive adsorbent that can effectively work at different pH conditions. Adsorption capacities of FS-400 for hydrolysed reactive dyes were ranging from 20–80% by weight of activated carbon. Capacities of this magnitude make adsorption attractive from the standpoint of economics and effective for removing reactive dyes.

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