Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Comparison of the Sorption of Anionic Dyes on Activated Carbon and Chitosan Derivatives from Dilute Solutions

Eric Guibal[a]; Peter McCarrick[b]; John M. Tobin[b]
[a] Ecole des Mines d'Alès, Laboratoire Génie de l'Environnement Industriel, Ales cedex, France [b] Dublin City University, School of Biotechnology, Dublin, Ireland

To cite this Article Guibal, Eric , McCarrick, Peter and Tobin, John M.(2003) 'Comparison of the Sorption of Anionic Dyes on Activated Carbon and Chitosan Derivatives from Dilute Solutions', Separation Science and Technology, 38: 12, 3049 — 3073

To link to this Article: DOI: 10.1081/SS-120022586

URL: http://dx.doi.org/10.1081/SS-120022586

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, Nos. 12 & 13, pp. 3049–3073, 2003

Comparison of the Sorption of Anionic Dyes on Activated Carbon and Chitosan Derivatives from Dilute Solutions

Eric Guibal,[1,*] Peter McCarrick,[1,2] and John M. Tobin[2]

[1]Ecole des Mines d'Alès, Laboratoire Génie de l'Environnement
Industriel, Ales cedex, France
[2]Dublin City University, School of Biotechnology, Dublin, Ireland

ABSTRACT

Activated carbon and chitosan were investigated for the sorption of several dyes. While the sorption on activated carbon was largely independent of the pH, the sorption of dyes on chitosan was controlled by the acidity of the solution. Anionic dye sorption onto chitosan occurred through electrostatic attraction on protonated amine groups. Sorption experiments were focused on dilute solutions and sorption capacities ranged between 200 and 2000 μmol g^{-1} for chitosan and between 50 and 900 μmol g^{-1} for activated carbon. Since, in most cases, equilibrium was reached within the first 12 hours of contact, sorption kinetics are relatively fast. However, both sorption capacities (sorption isotherms) and kinetics

---

*Correspondence: Eric Guibal, Ecole des Mines d'Alès, Laboratoire Génie de l'Environnement Industriel, 6, avenue de Clavières, F-30319 ALES cedex, France; E-mail: eric.guibal@ema.fr.

DOI: 10.1081/SS-120022586
0149-6395 (Print); 1520-5754 (Online)
www.dekker.com

depended on the type of dyes. The attempt to correlate sorption performance to the structure of the dye failed. Sorption kinetics are strongly influenced not only by intraparticle diffusion resistance but also by the affinity of the dye for the sorbent.

Key Words: Chitosan; Activated carbon; Anionic dyes; Sorption; Isotherms; Kinetics.

INTRODUCTION

Dyes are widely used in textile industry. Though most of the industrial dyes are nontoxic at the concentration discharged in the environment, the color they impart is very undesirable to the water user. Some of these dyes are also known for their potential health effect. So regulations are becoming progressively more stringent on their use and discharge. It is thus necessary to develop efficient processes for the recovery and the recycling, as far as possible, of such organic contaminants. Conventional processes, including precipitation, coagulation, or flocculation, have proved inefficient at removing usual dyes from dilute solutions. More sophisticated processes, such as photooxidation, have recently been proposed for the treatment of dye-containing effluents[1]; however, they are relatively expensive and not appropriate for the treatment of large flows. Biological processes have also been cited for the treatment of colored effluents.[2,3] Conversely, adsorption processes have been considered as potential processes for the decontamination of the effluents of textile industries. These processes are especially interesting since, in some cases, dyes can be selectively adsorbed, concentrated, and recycled. Many adsorbents have been tested during the last decades: mineral sorbents,[4,5] and activated carbon.[6–9] Though activated carbon has received a great deal of attention, due to its high efficiency and high sorption capacity, this sorbent is frequently nonselective and poorly reusable. There is still a need for the development of alternative sorbents, especially for low cost sorbents. Materials of biological origin, such as peat,[10] wood and related material,[11–14] and fungal biomass,[15,16] have been tested for the removal of organic and mineral contaminants. However, several reasons, such as variability in the composition, in the source, and low sorption capacities, have limited their use, despite their low cost. Chitosan is well known for its sorption properties. This biopolymer is extracted by a deacetylation procedure from chitin, the most abundant biopolymer in nature after cellulose. It is characterized by a high content of amine functions, which makes it very efficient at removing metal ions from dilute solutions through chelation or ion-exchange reactions, depending on pH and metal ions.[17−20] Published research is less abundant on the sorption of organic materials. Chitosan has been studied not only for the sorption of phenols,[21,22] humic acid,[23] pesticides,[24] and PCB,[25] but also for the removal of dyes.[26−36] Despite an increasing number of studies focusing on dye removal on chitin and chitosan, to date, there is not a systematic and comparative study taking into account the physicochemical properties of the different kinds of dyes.

The present work aims at comparing activated carbon and chitin/chitosan for the recovery of different types of dyes. Preliminary investigations were performed using activated carbon, chitosan, glutaraldehyde cross-linked chitosan, chitin, silica gel, and kieselfine (an organic-coated silica gel specially designed in the laboratory). Initial results showed that silica gel-based sorbents have relatively low-sorption capacities. The work was then focused on activated carbon (AC), chitin (Ch), chitosan (C), and glutaraldehyde cross-linked chitosan (for structure see Fig. 1). Cross-linked chitosan was prepared by reaction with glutaraldehyde to increase chitosan stability in acid solutions. Indeed, chitosan is soluble, for the most part, in mineral and organic acids, except in sulfuric acid solutions. Finally, studies have focused on chitosan and activated carbon for the determination of sorption isotherms and kinetics.

MATERIAL AND METHODS

Sorbents

Activated carbon was provided by Pica (France); it is referenced PICAFLO HP 150. It is an activated carbon especially tailored for the treatment of organic contaminants, macromolecules, colors, taste, and smells. It is a mesomacroporous activated carbon with a macroporous volume of $1.40\,\mathrm{cm^3\,g^{-1}}$ and a BET surface of $1100\,\mathrm{m^2\,g^{-1}}$. Ash content is 7% (maximum). The maximum coloring index was 150. The product was supplied as a fine powder (particle size lower 15 to 35 μm). Chitosan was supplied by Aber-Technologies (France) as a coarse powder, which was ground and sieved to use the 0- to 125-μm size fraction (fraction G1). For checking the influence of particle size, after grinding, the chitosan was sieved into several other size fractions: $125\,\mu m < G2 < 250\,\mu m$, $250\,\mu m < G3 < 500\,\mu m$, and $500\,\mu m < G4 < 710\,\mu m$. The deacetylation percentage and the molecular weight were previously determined at 87% and 125,000, respectively.[19] Chitin was provided as a coarse powder by Fluka (characteristics of the material were not determined). Chitosan cross linking

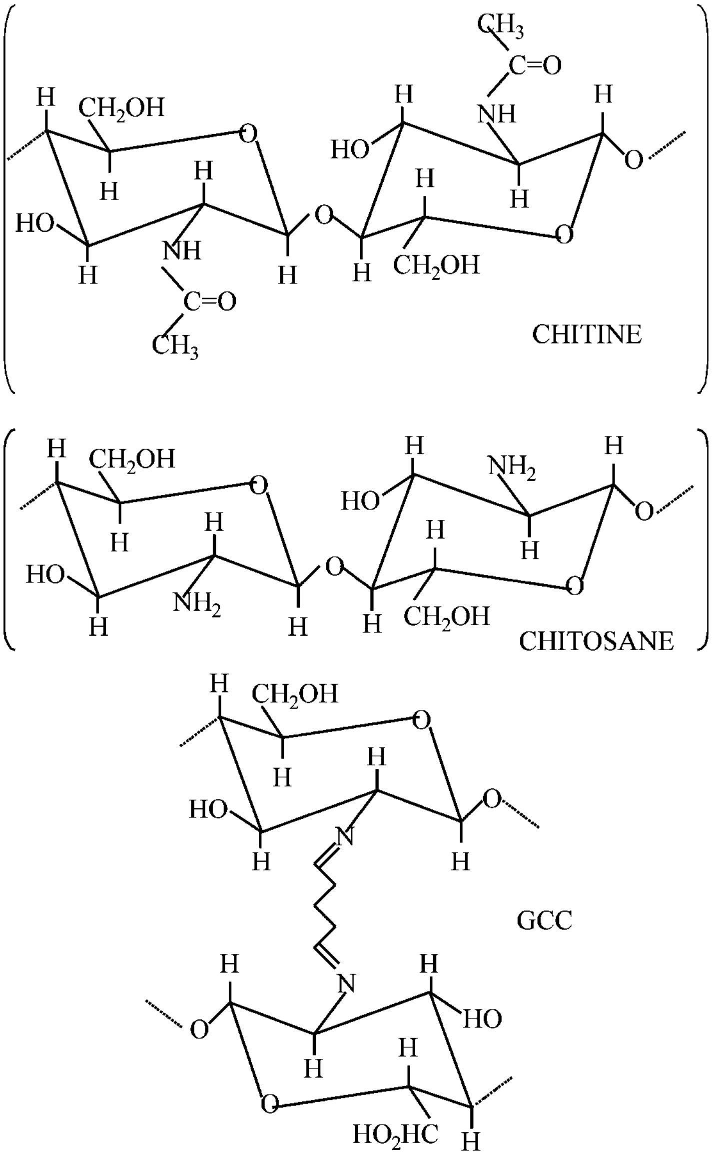


Figure 1. Structure of chitin, chitosan and GCC (glutaraldehyde cross-linked chitosan).

was performed by mixing the polymer with glutaraldehyde aqueous solution (5% w/w) for 16 hours. Glutaraldehyde amount was fixed to set an equimolar concentration in glutaraldehyde and amine functions. Finally, the cross-linking powder was rinsed several times to remove unreacted glutaraldehyde and dried at room temperature. Structure of biopolymers are reported in Fig. 1.

Dyes

Except Mordant Orange 10 (Sigma), dyes were supplied by Aldrich. These commercial products contained different percentages of pure dyes and a fraction of inert material that can represent up to 50% of the dye powder (Table 1 and Fig. 2). The actual fraction of pure dye is given and used in the discussion of experimental results. The calculation of sorption capacity took into account the actual concentration of dye in the powder.

Experimental Procedure

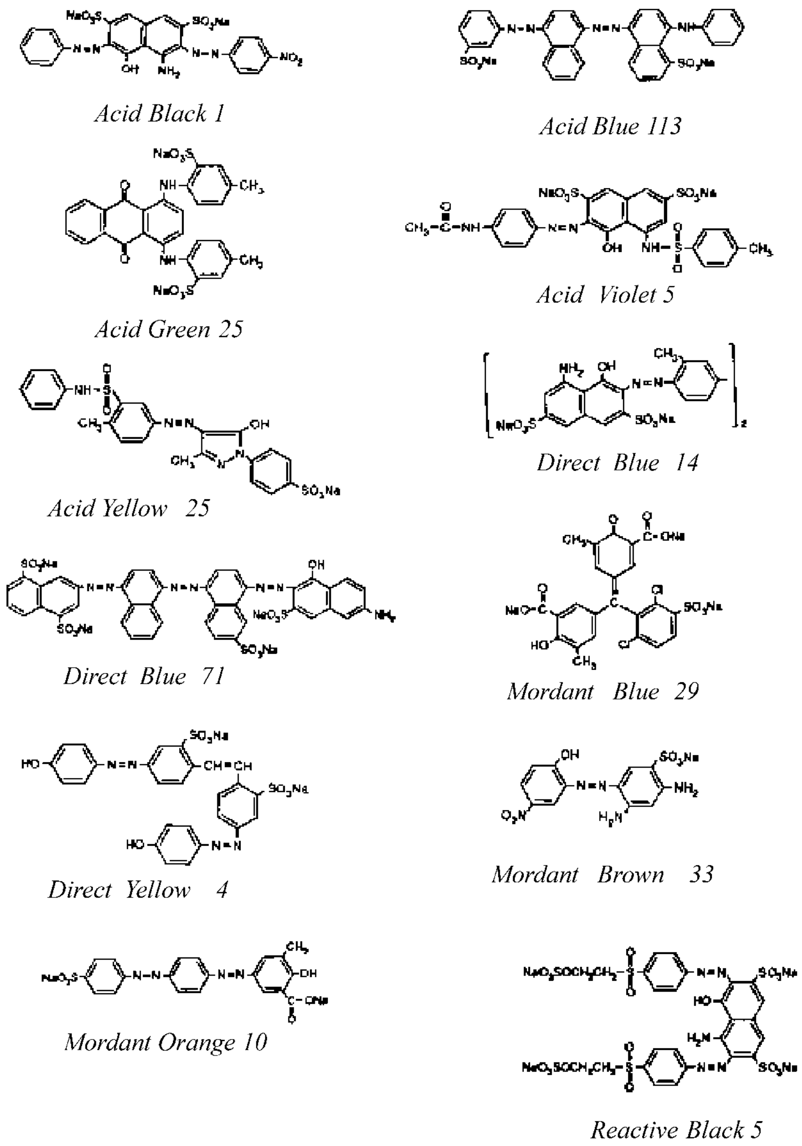
The influence of the pH on dye sorption was established using the following procedure: 50 mg of sorbent were brought into contact with 100 mL of solution containing a dye concentration of 100 mg L^{-1}, unless specified (including the inert material). The solutions were prepared at pH 4, pH 7, and pH 10 using buffered solutions prepared with predosed capsules (Bioblock Scientific (France), 1 capsule for 1 L). Additionally, an acid solution was prepared by dissolving the dye in a sulfuric acid solution adjusted to pH 1.5. Depending on the type of dye, some acid solutions were not experimented with, due to precipitation phenomena. Water–alcoholic mixtures for dye dissolving were not used to reduce the influence on hydrophilic and hydrophobic characteristics.

The contact between the sorbent and the solution lasted for 72 hours at least. This contact time proved sufficient to reach equilibrium in the case of metal ion sorption on chitosan. This was confirmed by sorption kinetics. Finally, the solutions were left to stand for 1 hour, and a sample was filtered on Whatman 1.2-μm filter membrane. The filtrate was analyzed for dye content by visible spectrophotometry using a SHIMADZU UV 160-A (Japan) at the optimum wavelength. Solutions were diluted as required for analysis and made using molar solutions of either sulfuric acid or sodium hydroxide, depending on the dye.

Table 1. Characteristics of selected dyes.

Dye	Color index number	Dye group	Purity (%)	Formula	Molecular weight ($g\,mol^{-1}$)
Acid black 1 (*naphthol blue black*)	20470	Acid diazo	80	$C_{22}H_{14}N_6Na_2O_9S_2$	616.50
Acid blue 113 (*sulfone cyanine 5R*)	26360	Anionic diazo	50	$C_{32}H_{21}N_5Na_2O_6S_2$	681.66
Acid green 25 (*alizarine cyanine green G*)	61570	Anionic anthraquinone	75	$C_{28}H_{20}N_2Na_2O_8S_2$	622.59
Acid violet 5 (*lanafuchsin 6B*)	18125	Anionic monoazo	50	$C_{25}H_{20}N_4Na_2O_{10}S_3$	678.63
Acid yellow 25 (*supranine yellow R*)	18835	Anionic monoazo	40	$C_{23}H_{20}N_5NaO_6S_2$	549.56
Direct blue 14 (*trypan blue*)	23850	Acid diazo	60	$C_{34}H_{24}N_6Na_4O_{14}S_4$	960.82
Direct blue 71 (*benzo light blue FFL*)	34140	Anionic triazo	50	$C_{40}H_{23}N_7Na_4O_{13}S_4$	1029.9
Direct yellow 4 (*brilliant yellow*)	24890	Anionic diazo	70	$C_{26}H_{18}N_4Na_2O_8S_2$	624.56
Mordant blue 29 (*chrome azurol S*)	43825	Triphenyl methane	65	$C_{23}H_{13}Cl_2Na_3O_9S$	605.29
Mordant brown 33 (*acid anthracene brown RH*)	13250	Monoazo	60	$C_{12}H_{10}N_5Na_2O_8S$	375.27
Mordant orange 10	26560	Acid diazo	60	$C_{20}H_{14}N_4Na_2O_6S$	484.4
Reactive black 5 (*remazol blue black*)	20505	Diazo reactive vinylsulfonyl	55	$C_{26}H_{21}N_5Na_4O_{19}S_6$	991.82

Sorption kinetic experiments were performed by mixing 400 mg of sorbent with 1 L of dye solution, with a concentration of $100\,mg\,L^{-1}$ (including the inert material), unless specified, using an agitated vessel (magnetic agitator). Samples were regularly withdrawn, filtered, and analyzed.



Acid Black 1

Acid Blue 113

Acid Green 25

Acid Violet 5

Acid Yellow 25

Direct Blue 14

Direct Blue 71

Mordant Blue 29

Direct Yellow 4

Mordant Brown 33

Mordant Orange 10

Reactive Black 5

Figure 2. Structure of selected dyes.

Sorption isotherms were obtained by mixing for 72 hours on a reciprocal shaker increasing amounts of sorbent with a fixed volume of solution at known initial dye concentrations. After filtration and analysis, the residual concentration was used to determine the amount of dye adsorbed on the support, using the mass-balance equation.

RESULTS AND DISCUSSION

Influence of pH on Dye Sorption

Table 2 reports sorption capacities for activated carbon, chitosan, chitin, and cross-linked chitosan for the recovery of selected dyes under specific experimental conditions at pH 1.5, pH 4, pH 7, and pH 10. Under these experimental conditions, the sorbents did not reach similar saturation levels; therefore, it is not possible to directly compare efficiencies of the sorbents. However, these results are sufficient to determine the optimum pH range and to define the influence of the pH on sorption efficiency for selected dyes and for each sorbent.

Activated Carbon

Table 2 shows that for most of the selected dyes, the sorption capacity was independent of the pH. The only significant exception is Mordant Blue 29, for which the sorption capacity significantly decreases at increasing pH. This dye belongs to the arylmethane family of dyes; its structure is different to that of the other selected dyes. It bears two carboxylic acid functions and one sulfonic group. Mordant Orange 10 also bears one sulfonic group and one carboxylic-acid function, but the sorption of the dye was not influenced by the pH in this case. The difference in the sorption behavior may be due to the different effect of the dye backbone rather than to the ionic groups. Al-Degs et al compared sorption properties of different kinds of activated carbon for two anionic dyes and one cationic dye.[8] They observed that these activated carbons have a preferred adsorption of cationic dye over anionic ones, and two of these sorbents where unable to sorb anionic dyes. These two activated carbons were characterized by a higher surface acidity and a lower surface basicity. The influence of the surface properties of activated carbon on dye sorption had been explained by electrostatic attraction between the dye charge and adsorbent surface

Table 2. Influence of pH on the sorption capacities (mg g^{-1}) of selected dyes using activated carbon (AC), chitosan (Ch), cross-linked chitosan (CC) and chitin (Chi).[a]

	pH 1.5				pH 4				pH 7				pH 10			
Dye	AC	Ch	CC	Chi	AC	Ch	CC	Chi	AC	Ch	CC	Chi	AC	Ch	CC	Chi
ABa 1	197	189	76	81	191	181	37	60	184	185	17	34	187	22	0	9
AG 25	194	193	166	95	196	194	138	95	195	179	86	48	191	34	35	59
AV 5	196	157	194	92	*207*	202	140	72	*200*	152	24	29	*199*	0	0	6
AY 25	*177*	171	144	157	*183*	179	124	150	*200*	179	86	121	*165*	0	1	2
DB 71	—	—	—	—	85	143	14	109	79	101	1	69	77	77	8	44
MBu 29	197	192	114	38	164	58	48	32	82	37	1	0	20	0	0	0
MBr 33	—	—	—	—	197	188	130	74	*200*	91	12	16	187	0	0	0
MO 10	—	—	—	—	*219*	215	103	78	199	157	1	25	205	9	4	4
RB 5	*201*	*201*	198	92	*213*	*213*	99	71	*200*	*200*	6	63	*180*	121	3	52

Dye concentration 50 mg L^{-1}; *Italics*: Experimental conditions lead to a residual dye concentration tending to 0, the sorption capacity may be higher since the sorbent is not saturated; —The dye was not soluble at this pH controlled with sulfuric acid.

[a] Standard experimental conditions: dye concentration: 100 mg(salt) L^{-1} (the percentage of inert material has not been taken into account in the calculation of sorption capacity), volume of solution 100 mL, sorbent mass: 50 mg, unless specified.

charge (usually negative for mineral sorbents,[4] or agriculture by-products.[37,38]) In the present work, with the exception of Mordant Blue 29, anionic dyes were readily adsorbed, and the sorption was not influenced by the pH. The weak effect of pH on dye-sorption properties can be explained by the diversity of surface groups (carboxylic, lactonic, phenolic, carbonyle, and etheric groups) that make the chemistry (acid–base character) much more versatile than that of other adsorbents. Juang and Swei[39] also observed that the sorption properties on activated carbon strongly depend on the nature of the dye.

Chitosan

In the case of chitosan, dye sorption was favored in acidic solutions. Indeed, in acid solutions, the protonation of amine groups gives to the polymer a cationic behavior that leads to electrostatic attraction of anions.[26–29] Chitosan is characterized by the deacetylation degree of the biopolymer; increasing the deacetylation degree involves an increase in the relative proportion of amine groups, which are able to be protonated. The intrinsic pK_a of chitosan has been shown to range between 6.4 and 7.1, depending on the degree of deacteylation and the degree of neutralization of protonated-amine functions, according to the Katchalski equation.[40] For the sample used in this study (with a deacetylation degree of 87%), the intrinsic pK_a is assumed to be close to 6.5. Consequently, below pH 6.5, chitosan can be considered as a cationic support. This property will influence the sorption procedure, depending on the charge (and functions) of the dye under the corresponding experimental conditions (pH). However, the change in the sorption capacity depends on the dye. Mordant Blue 29 sorption was characterized by a continuous and significant decrease in the sorption capacity with increasing the pH. For Reactive Black 5, sorption capacity was almost unchanged at increasing the pH. For the other dyes (soluble at pH 1.5), sorption capacities were comparable at pH 1.5 and pH 4; while at pH 7, they began to weakly decrease for Acid Black 1, Acid Green 25, Acid Yellow 25, and, more significantly, for Direct Blue 71, Mordant Blue 29, Mordant Brown 33, and Mordant Orange 10. At pH 10, sorption capacity tended to 0 for Acid Violet 5, Acid Yellow 25, Mordant Blue 29, Mordant Brown 33, and Mordant Orange 10, while for the other dyes, a low sorption capacity was maintained.

Juang et al[34] compared the sorption of reactive dyes on chitosan to that on cellulose materials and suggested that dye immobilization occurs on hydroxyl groups. Muzzarelli and co-workers studied the interactions of dyes (anionic and cationic) with chitosan in solution by circular dichroism analysis.[31] They observed that the pH of the solution changed both the extent and the mode of the binding, and they explained this change in the mechanism by changes in the conformation of the polymer chains. They also observed that chitosan was not able to react with cationic dyes at pH 5 to 6. Chitosan exhibits a reciprocal trend regarding dye sorption compared to activated carbon. Giles et al reported that dye sorption occurred through hydrogen bonding with dyes and/or electrostatic interactions with acetamide groups on chitin.[41] However, Lee et al observed that the dye binding efficiency was significantly higher for chitosan than that of chitin.[42] The influence of the pH on anionic dye sorption confirms the electrostatic interaction between chitosan and selected dyes. The differences between the dyes may be due to different pK_as or, alternatively, to the contribution of other sorption mechanisms, including hydrophilic and hydrophobic interactions. For example, Giles et al reported that increasing the size of the aromatic portion of dye molecules increases the adsorption efficiency.[41]

Chitin and Cross-Linked Chitosan

The sorption of dyes onto chitin followed the same trend as that of chitosan, but the sorption level was significantly lower. The presence of acetyl groups limited the accessibility to protonated-amine sites and then reduced the sorption capacities. Depending on the pH and the dye, the reduction in sorption capacity decreased by two to threefold. The sorption is not solely due to protonated amine sites. The variation in sorption properties is not proportional to deacetylation degree, and it changes with the type of dye. Amide and hydroxyl groups can also be involved in dye fixation. In the case of cross-linked chitosan, similar trends were observed; however, the sorption capacity can be higher or lower than that of chitin depending on the dye and the pH.

At pH 10, both chitin and cross-linked chitosan poorly sorbed selected dyes, with the exception of Acid Green 25, Direct Blue 71, and Reactive Black 5, for which a residual sorption capacity was observed; for other dyes, sorption levels were nonsignificant. Dyes can be classified into two groups depending on the better efficiency of chitin or cross-linked chitosan. Whatever the pH (1.5, 4 and 7), chitin sorption was better than that of cross-linked chitosan for Acid Black 1, Acid Yellow 25, Direct Blue 71; while for the other dyes, cross-linked chitosan exhibited higher sorption capacities than chitin. This classification can be only partially correlated to that obtained with chitosan.

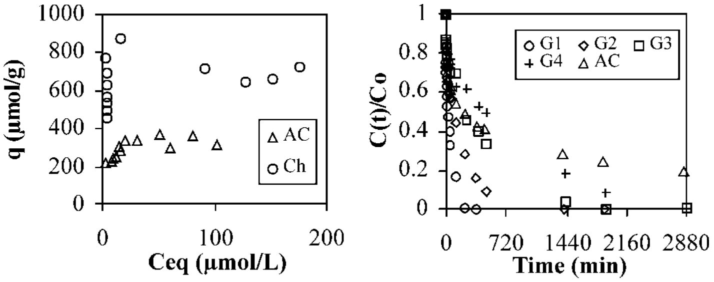


Figure 3. Acid Black 1 sorption isotherms for activated carbon (AC) and chitosan (Ch) and uptake kinetics (AC, chitosan G1, G2, G3, G4) at pH 3.

At this stage, it seems difficult to predict sorption properties on the simple basis of dye structure.

Sorption Isotherms

Figures 3 through 13 present the sorption isotherms for selected dyes using chitosan and activated carbon. Table 3 reports the maximum sorption capacities of both activated carbon and chitosan for selected dyes (the data for sorption capacities were corrected taking into account the actual fraction of active dye in the commercial salt). The maximum sorption capacity strongly depends on the sorbent and the dye. Chitosan exhibited a twofold, or more, increase in the sorption capacity compared to activated carbon in the case of Acid Black 1, Acid Green 25, Direct Blue 14, Reactive Black 5, Mordant Brown 33, and Mordant Orange 10. In the case of Direct Yellow 4, a similar

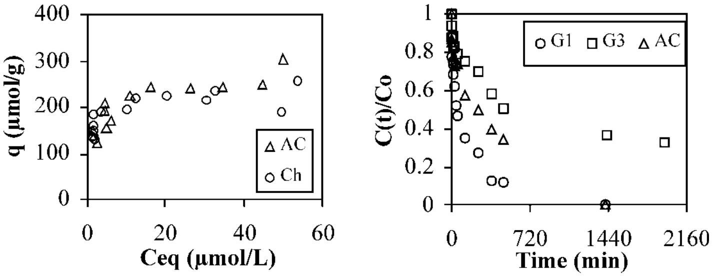


Figure 4. Acid Blue 113 sorption isotherms for activated carbon (AC) and chitosan (Ch) and uptake kinetics (AC, chitosan G1 and G3) at pH 3.

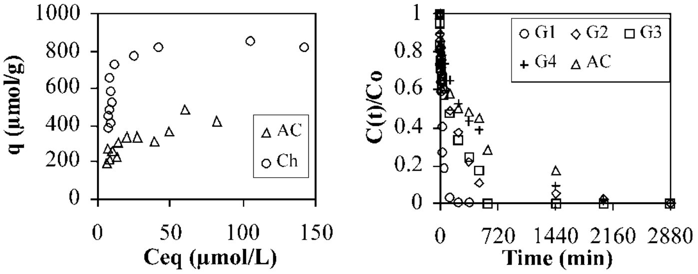


Figure 5. Acid Green 25 sorption isotherms for activated carbon (AC) and chitosan (Ch) and uptake kinetics (AC, chitosan G1, G2, G3, G4) at pH 3.

difference in the sorption capacities of the two sorbents has been observed at low residual concentration, while at higher dye concentration, the sorption isotherm curve presented a sigmoidal curve (BET-type isotherm) close to that observed by Yoshida et al for the sorption of Acid Orange II on cross-linked chitosan fibers.[30] They observed an unfavorable isotherm at near-neutral pH; while in acid solutions, the isotherms were modeled using the Langmuir equation, though they are almost rectangular. At pH close to the neutrality, they successfully used the BET equation for finite number of layers. At high relative residual concentration, the sorption capacity sharply increased close to the value obtained with chitosan. Similar sorption capacities were also obtained with Acid Blue 113 and Acid Violet 5 for both activated carbon and chitosan. On the other hand, for Acid Yellow 25 and Mordant Blue 29, activated carbon exhibited a sorption capacity that was 50 to 100% greater than that of chitosan. The sorption capacities reported in Table 3 are significantly lower than those cited by other studies,[26–29] but the present

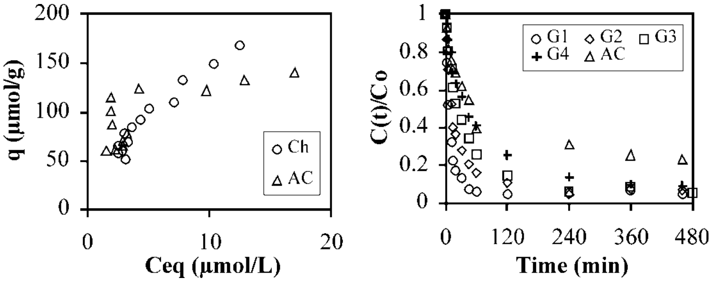


Figure 6. Acid Violet 5 sorption isotherms for activated carbon (AC) and chitosan (Ch) and uptake kinetics (AC, chitosan G1, G2, G3, G4) at pH 3.

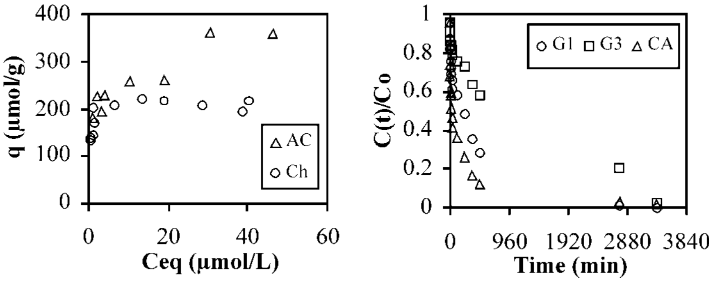


Figure 7. Acid Yellow 25 sorption isotherms for activated carbon (AC) and chitosan (Ch) and uptake kinetics (AC, chitosan G1, G2, G3, G4) at pH 3.

study was focused on low dye concentrations. One would expect higher sorption capacities for higher concentration ranges, taking into account the condensation phenomena that could occur such as in sorption processes described by the BET isotherm equation. Another parameter that may explain the low sorption capacities and the variability observed in some experimental series is that the pH of the solution was not controlled along the sorption process, and final pH was monitored at the end of the experiments showing that the final pH can be increased by 2 pH units. Such a high increase in the pH may cause unfavorable experimental conditions for the sorption of the dyes on chitosan; the previous section showed that at near-neutral pH, the sorption capacity began to significantly decrease for the majority of the dyes investigated. Thus, one could expect an increase in the sorption capacities by controlling the pH over the sorption process.

Taking into account the deacetylation degree of the chitosan used for this study, it appears that free amine content in the polymer is about

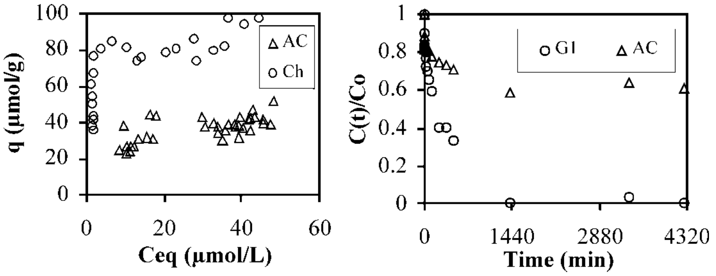


Figure 8. Direct Blue 14 sorption isotherms for activated carbon (AC) and chitosan (Ch) and uptake kinetics (AC, chitosan G1, G2, G3, G4) at pH 3.

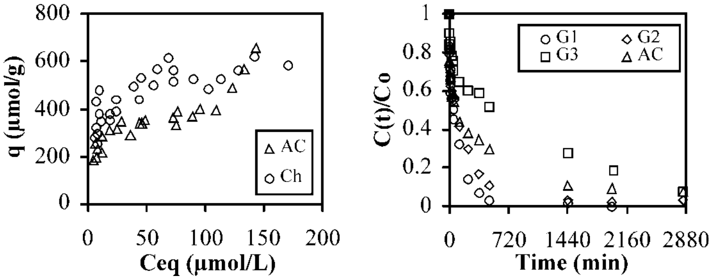


Figure 9. Direct Yellow 4 sorption isotherms for activated carbon (AC) and chitosan (Ch) and uptake kinetics (AC, chitosan G1, G2, G3, G4) at pH 3.

5.2 mmol -NH_2 g^{-1} (6 mmol N g^{-1}). Although we are not sure that the sorbent was fully saturated under selected experimental conditions, it is possible to say that for the majority of cases, sorption capacity was between 200 to 2000 µmol g^{-1}. It leads to a mean molar ratio between the dye and the amine groups of 1:12 (1:3 and 1:4 in the case of Mordant Brown 33 and Mordant Orange 10, respectively). It is far from the levels reached with some metal anions, which were also sorbed through electrostatic attraction on chitosan in acid solutions. For platinum, palladium, molybdate, and vanadate, the sorption capacity ranged between 3 and 7 mmol Me g^{-1}, ca. 1:2 to 1.2:1 molar ratios between metal ions and amine groups (and these ratios are underestimated since the fraction of polymer constituted by the glutaraldehyde, used for chitosan cross-linking, was not taken into account in the calculation).[19–20,43] Maghami and Roberts[29] postulated a 1:1 stoichiometry for the interaction of sulfonic acid groups on the dyes with protonated amine groups of the chitosan for mono-, di-, and trisulfonated dyes, working with concentrations of dyes as

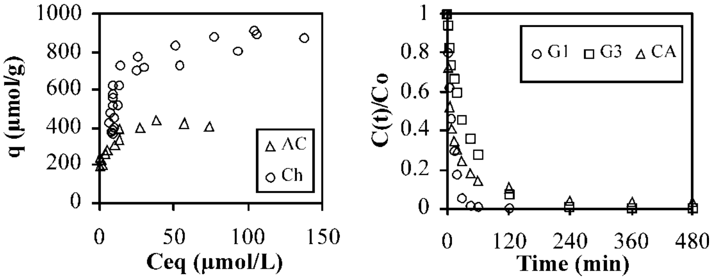


Figure 10. Mordant Blue 29 sorption isotherms for activated carbon (AC) and chitosan (Ch) and uptake kinetics (AC, chitosan G1, G2, G3, G4) at pH 3.

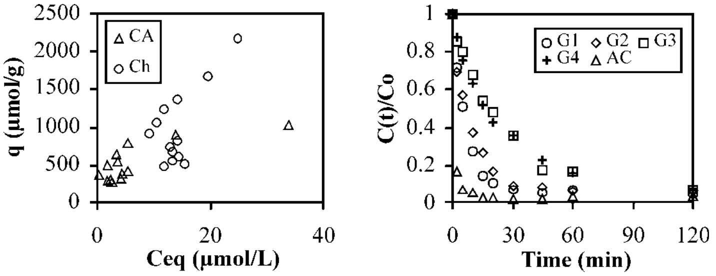


Figure 11. Mordant Brown 33 sorption isotherms for activated carbon (AC) and chitosan (Ch) and uptake kinetics (AC, chitosan G1, G2, G3, G4) at pH 3.

high as 5-mmol dye L^{-1}, with a chitosan dosage of 0.5 or 1 g L^{-1} in 0.083-M aqueous acetic acid solutions. Bearing in mind the nonsaturation of the sorbent and the pH variation, we attempted to correlate, when relevant, the sorption capacities of the dyes to their sulfonate content according to Maghami and Roberts findings. However, no meaningful correlation was apparent: some dyes containing numerous sulfonic acid groups (ca. two to four groups per molecule) exhibited sorption capacities lower than some dyes containing only one group per molecule. So the prediction of sorption capacities from only sulfonic acid content is not possible, and other parameters may control sorption capacities: pK_as, presence of other functional groups, and so forth. In the case of activated carbon, it was also impossible to correlate the sulfonic content of the dyes to their sorption capacity. The diversity of functional groups present on activated carbon may explain this observation.[8]

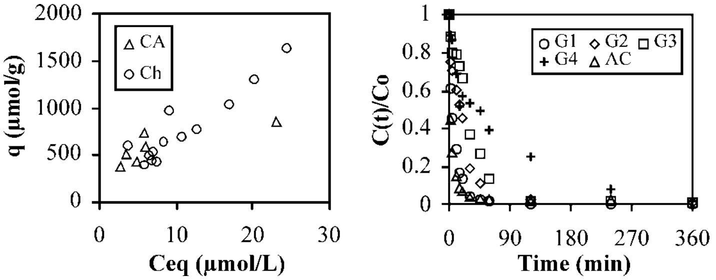


Figure 12. Mordant Orange 10 sorption isotherms for activated carbon (AC) and chitosan (Ch) and uptake kinetics (AC, chitosan G1, G2, G3, G4) at pH 3.

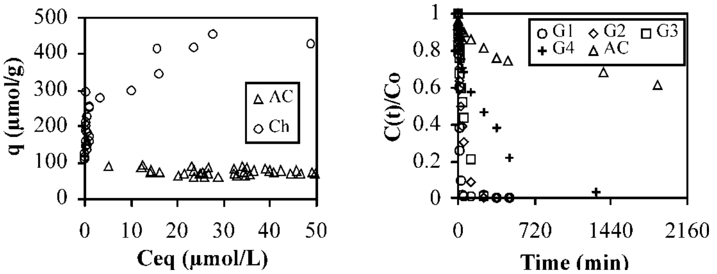


Figure 13. Reactive Black 5 sorption isotherms for activated carbon (AC) and chitosan (Ch) and uptake kinetics (AC, chitosan G1, G2, G3, G4) at pH 3.

Sorption Kinetics

Figures 3 through 13 present the sorption kinetics for activated carbon and chitosan particles. Table 3 summarizes the time required to reach half the initial dye concentration. Sorption kinetics are usually controlled by different

Table 3. Summary of sorption performance.

	Maximum sorption capacity (μmol g^{-1})		Time for half reduction of the initial concentration (min)				
Dye	AC	Ch	AC	G1	G2	G3	G4
Acid black 1	370	800	210	25	90	230	480
Acid blue 113	250	250	240	50	—	480	—
Acid green 25	450	850	240	25	120	110	280
Acid violet 5	130	160	50	6	12	22	37
Acid yellow 25	360	220	35	220	—	720	—
Direct blue 14	50	90	NR	180	—	—	—
Direct yellow 4	380 700[a]	620	80	45	90	500	420
Mordant blue 29	890	420	7	9	—	28	—
Mordant brown 33	1000	2000	1	6	8	17	16
Mordant orange 10	850	1600	1	4	17	25	45
Reactive black 5	95	440	3 days	13	30	50	220

[a] The saturation of the sorbent was not reached and the curve was characterized by a BET-shape. The first number shows the sorption capacity at the first plateau while the second number shows the sorption capacity reached at high residual dye concentration (in the vertical asymptotic region).

mechanisms, of which the most limiting are the diffusion mechanisms, including the external and the intraparticle mass-transfer resistances and the reaction rate. As a first approximation, external diffusion controls the initial stage of the sorption process, while the second stage of the process is controlled by the intraparticle diffusion. McKay observed that the diffusion within the particle is much slower than the movement of the dye from solution to the external solid surface because of the greater mechanical obstruction to movement presented by the surface molecules or surface layers and also because of the restraining chemical attractions between dye and adsorbent.[6] During adsorption of the dye from a well-stirred tank, dye molecules arrive at the adsorbent surface more rapidly than they can diffuse away in the solid. The dye accumulates at the surface and a pseudo-equilibrium is established, and further adsorption of dye can take place only at the same rate as the surface concentration is depleted by inward adsorption. He correlated the dye uptake to the square root of time over a large adsorption zone to get the diffusivity of the dye in activated carbon particles. It is possible to define a rate parameter by plotting the sorption capacity as a function of the square root of time.[6,44] Several different steps in the process have also been characterized by this simple mathematical modeling: different linear sections have been identified in the sorption of some reactive dyes on chitosan.[34]

Comparison of Sorption Kinetics for Activated Carbon and Chitosan

The dyes can be classified in three groups in respect to sorption kinetics for activated carbon and chitosan of the smallest particles (to get comparable experimental conditions relative to particle size effect). Class I corresponds to those dyes for which sorption on activated carbon was significantly faster than chitosan. Class II are the dyes for which sorption was comparable for each sorbent, while the other dyes for which chitosan was much more efficient than activated carbon are compiled in Class III. This ranking was performed on the half-time criteria: the segregation criteria were ratio of half-time for activated carbon and chitosan of 2 and 1/2, for Class III and Class I, respectively. In Class I, it is possible to report, on the basis of Table 3, Acid Yellow 25, Mordant Brown 33, and Mordant Orange 10. In Class II, we identified Direct Yellow 4 and Mordant Blue 29; while in Class III, dyes included Acid Black 1, Acid Blue 113, Acid Green 25, and Direct Blue 14. In an attempt to define a predictive strategy for the selection of the best sorbent, this classification was compared to the type of the dyes. However, it was difficult to directly correlate the structure of the dye with the sorption kinetics. Though most of the acid diazo dyes have been classified in the Class III group (four over six), two of them were reported in Class I and Class II. Anionic monoazo dyes were preferentially classified in Class I.

The external diffusion depends on several parameters, including the external surface area of the sorbent, which is mainly controlled by the particle size, the shape,and density of the particles, the concentration of the solution, and the agitation velocity. Since the particle size was comparable for chitosan and activated carbon sorbents, the velocity of agitation and the dye concentration were identical in these experiments, and the influence of external diffusion is expected to be minimum and not sufficient to explain the great differences observed between the sorbents. Intraparticle diffusion is usually controlled by the porosity (porous distribution, pore volume, pore size) of the particle. The greater the particle size, the greater the contribution of intraparticle diffusion resistance in the control of the sorption kinetics for low porous materials. Activated carbon is characterized by a large superficial area and a great porosity that limit the resistance to intraparticle diffusion. Walker and Weatherley[43] compared the adsorption of dyes on activated carbon and bone char for three different dyes and observed that sorption isotherms are controlled by the distribution of sorbent pore size and by a phenomenon of dye aggregation. The aggregation of dyes molecules may involve a strong increase in the size of the diffusing molecule; this effect may be reinforced by the influence of pore size in controlling intraparticle diffusion properties and accessibility to internal sites. Juang et al[45] also correlated the efficiency in adsorbing phenols and dyes onto activated carbon to their surface characteristics (external surface and contribution of micropores). It may be important for activated carbon, but a more stringent effect is expected for chitosan since this polymer is characterized by a low superficial area and a low porosity that can control the diffusion to the center of the particles, especially in the case of the diffusion of large molecules. In the present case, there is not a correlation between the size of the dye and the better efficiency of chitosan for its sorption compared to activated carbon; the porosity of the sorbent and the superficial area do not control the sorption kinetics. On the other hand, it is possible to see that Class III dyes, in the most cases but not systematically, exhibited a higher maximum sorption capacity on chitosan than on activated carbon. Those dyes for which the maximum sorption capacity was higher for activated carbon than for chitosan were more rapidly sorbed on activated carbon than on chitosan. The affinity of the sorbent for the dye, given as proportional of the initial slope of the sorption isotherms and representative of the strength of the interaction, seems to be an important criterion not only for sorption isotherms but also for uptake kinetics.

However, it is important to note that a direct comparison of sorption kinetics for different dyes is not possible, since the actual concentration (taking into account the presence of the inert material) was not exactly the same for all the dyes and that the level of saturation was not the same for each system. Indeed, for some systems (dye–sorbent) characterized by a high affinity, the residual concentration quickly tended to 0 without the saturation of the sorbent.

Influence of Chitosan Particle Size on Sorption Kinetics

As expected, both the half-time and the time required to reach the equilibrium increased by increasing the size of sorbent particles. It is interesting to observe that for the dyes for which the sorption was faster for chitosan than for activated carbon (G1 particles) sorption rates were comparable to those of activated carbon for larger particles (size fractions G2 and G3). When the dyes have strong interactions with chitosan, this sorbent allows larger particle size of sorbents to be used to get the same sorption rate: it is especially important for large-scale applications since it is easier to manage large sorbent particles rather than fine powders. For those dyes for which the affinity is significantly lower for chitosan than for activated carbon, increasing the particle size involves a strong decrease in the kinetics that limits the interest in using chitosan sorbents. It could be interesting to use chitosan gel beads instead of flakes since the production of chitosan gel beads decreases the residual crystallinity of chitosan. Moreover, this enhances both the porosity and the diffusion properties of the polymer (due to the expansion of the polymer network and the increase in the specific surface), as it was previously observed for metal ion and dye sorption.[35,46] The strong effect of particle size confirms that the contribution of intraparticle diffusion resistance on the control of kinetics cannot be neglected. However, the affinity of the dye for the sorbent changes the relative importance of the intraparticle diffusion on the control of the overall kinetics.

A more complete study would be necessary to discuss more accurately the predominant controlling mechanism, more specifically the following parameters should simultaneously be varied: particle size, agitation velocity, and dye concentration.

Treatment of a Wastewater from Textile Industry

Figure 14 shows the change in the relative optical density at three different wavelengths of the solution put into contact with chitosan (G1 and G3 fractions) and activated carbon. The presence of several dyes in the industrial effluent required the measurement of a color index according the norm EN ISO 7887 (Section III)[47]; this includes the determination of the optical density at $\lambda = 436$ nm, $\lambda = 525$ nm, and $\lambda = 620$ nm. Experiments have been performed at pH 3 with chitosan sorbents

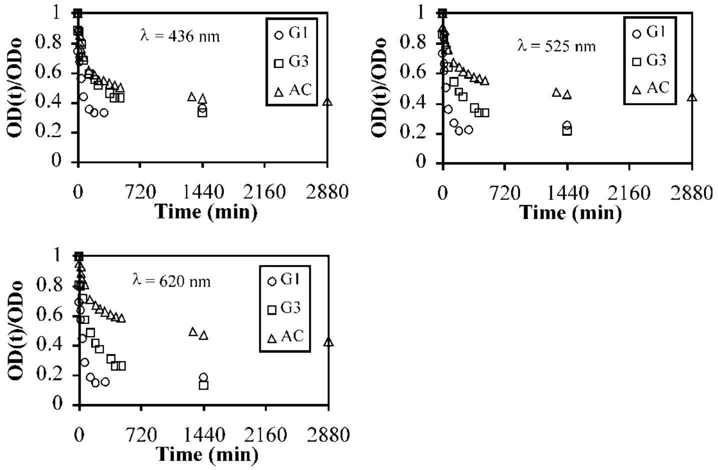


Figure 14. Adsorption of dyes from a textile industry wastewater: time course of the relative optical density of the solution at three different wavelengths (AC: Activated carbon, G1, G3 chitosan samples).

(controlled with sulfuric acid) and pH 8 (natural pH of the solution). For activated carbon, the pH was not changed since our previous findings had shown that sorption was not influenced by the pH between pH 3 and the near neutrality. It is obvious that the chitosan sorbents were significantly more efficient than activated carbon by decreasing the absorbance of the solutions. It was especially significant for λ = 525 nm, and λ = 620 nm, whatever the size of the chitosan particles; while at λ = 436 nm, the kinetic curves of activated carbon and G3 were overlapped. Moreover, it appears that a fraction of the dyes was refractory to the sorption on chitosan, between 15 and 30%, depending on the wavelength. For the sorption on activated carbon, 40 to 50% of the dyes were not removed from the solution. Chitosan appeared to be more appropriate than the selected activated carbon for the treatment of this industrial effluent on the basis of sorption equilibrium but also on uptake kinetics. Indeed, at similar particle sizes (0 to 125 μm), equilibrium was reached within the first 3 hours of contact with chitosan G1 (24 hours with G3), while 48 hours were necessary in the case of activated carbon.

CONCLUSION

The sorption of dyes, for the majority of dyes investigated in this study, is independent of the pH in the case of activated carbon. Acid solutions are required for the sorption of dyes on chitosan. In acid solutions, amine functions on chitosan are protonated and subjected to electrostatic attraction of dye anions, mainly on sulfonic acid groups, though sorption performance cannot be directly correlated to the sulfonic acid content of the dye. This prediction is made complex by the diversity of functional groups born by the dyes. Sorption kinetics are controlled by intraparticle diffusion resistance, but the affinity of the dye for the sorbent also plays an important role on the kinetic control.

The best choice for the sorbent between activated carbon and chitosan depends on the dye. It was impossible to determine a correlation between the chemical structure of the dye and its affinity for either activated carbon or chitosan. It may be necessary to complete the characterization of the dyes by determining complementary physicochemical properties, such as their pK_as and their hydrophobicity (through for example the octanol–water index) in an attempt to correlate these properties to the efficiency of dye extraction efficiency by activated carbon and chitosan. This study is currently under investigation.

ACKNOWLEDGMENTS

The authors are indebted to the Leonardo program from the EU and to the company France Chitine for financial support for the trainee fellowship of Peter McCarrick. The authors thank Sveinung Ryen for his working assistance.

REFERENCES

1. Arslan, I.; Balcioglu, A. Advanced oxidation of raw and biotreated textile industry wastewater with O_3, H_2O_2/UV-C and their sequential application. J. Chem. Technol. Biotechnol. **2001**, *76*, 53–60.
2. Walker, G.M.; Weartherley, L.R. Biological activated carbon treatment of industrial wastewater in stirred tank reactors. Chem. Eng. J. **1999**, *75*, 201–206.
3. Fu, L.-Y.; Wen, X.-H.; Lu, Q.-L.; Qian, Y. Treatment of dyeing wastewater in two SBR systems. Proc. Biochem. **2001**, *36*, 1111–1118.
4. Sethuraman, V.V.; Raymahashay, B.C. Color removal by clays. Kinetic study of adsorption of cationic and anionic dyes. Environ. Sci. Technol. **1975**, *9* (13), 1139–1140.
5. McKay, G. The adsorption of basic dyes onto silica from aqueous solution–solid diffusion model. Chem. Eng. Sci. **1984**, *39* (1), 129–138.

6. McKay, G. The adsorption of dyestuffs from aqueous solutions using activated carbon. III. Intraparticle diffusion process. J. Chem. Technol. Biotechnol. **1983**, *33A*, 196–204.
7. Yang, X.-Y.; Ad-Duri, B. Application of branched pore diffusion model in the adsorption of reactive dyes on activated carbon. Chem. Eng. J. **2001**, *83*, 15–23.
8. Al-Degs, Y.; Kraisheh, M.A.M.; Allen, S.J.; Ahmad, M.N.A. Sorption behavior of cationic and anionic dyes from aqueous solution on different types of activated carbon. Sep. Sci. Technol. **2001**, *36* (1), 91–102.
9. McKay, G. Solution to the homogeneous surface diffusion model for batch adsorption systems using orthogonal collocation. Chem. Eng. J. **2001**, *81*, 213–221.
10. Allen, S.J.; McKay, G. Diffusion model for the sorption of dyes on peat. J. Sep. Proc. Technol. **1987**, *8*, 18–25.
11. Nassar, M.M.; El-Geundi, M.S. Comparative cost of colour removal from textile effluents using natural adsorbents. J. Chem. Technol. Biotechnol. **1991**, *50*, 257–264.
12. Chen, B.; Hui, C.W.; McKay, G. Pore-surface diffusion modeling for dyes from effluent on pith. Langmuir **2001**, *17*, 740–748.
13. Waly, A.; Abdel-Mohdy, F.A.; Aly, A.S.; Hebeish, A. Synthesis and characterization of cellulose ion exchanger. II. Pilot scale and utilization in dye-heavy metal removal. J. Appl. Polym. Sci. **1998**, *68*, 2151–2157.
14. Nigam, P.; Armour, G.; Banat, I.M.; Singh, D.; Marchant, R. Physical removal of textile dyes from effluents and solid-state fermentation of dyes-adsorbed agricultural residues. Biores. Technol. **2000**, *27*, 219–226.
15. Christov, L.P.; van Driessel, B.; du Plessis, C.A. Fungal biomass from *Rhizomucor pusillus* as adsorbent of chromophores from a bleach plant effluent. Proc. Biochem. **1999**, *35*, 91–95.
16. Aksu, Z.; Tezer, S. Equilibrium and kinetic modelling of biosorption of remazol black B by *Rhizopus arrhizus* in a batch system: effect of temperature. Proc. Biochem. **2000**, *36*, 431–439.
17. Domard, A. pH and C.D. Measurements on a fully deacetylated chitosan: application to Cu(II)-polymer interactions. Int. J. Biol. Macromol. **1987**, *9*, 98–104.
18. Inoue, K. Application of chitosan in separation and purification of metals. In: *Recent Advances in Marine Biotechnology, Volume 2, Environmental Marine Biotechnology*; Fingerman, M., Nagabhushanam, R., Thompson, M.-F., Eds.; Oxford & IBH Publishing PVT, Ltd.: New Delhi, India, 1998; 63–97.

19. Guibal, E.; Larkin, A.; Vincent, T.; Tobin, J.M. Chitosan sorbents for platinum sorption from dilute solutions. Ind. Eng. Chem. Res. **1999**, *38*, 401–412.
20. Guibal, E.; Milot, C.; Roussy, J. Influence of hydrolysis mechanisms on molybdate sorption isotherms using chitosan. Sep. Sci. Technol. **2000**, *35* (7), 1021–1038.
21. Xing, B.; McGill, W.B.; Dudas, M.J.; Maham, Y.; Hepler, L. Sorption of phenol by selected biopolymers: isotherms, energetics, and polarity. Environ. Sci. Technol. **1994**, *28* (3), 466–473.
22. Popa, M.-I.; Aeleni, N.; Popa, V.I.; Andrei, D. Study of the interactions between polyphenolic compounds and chitosan. React. Funct. Polym. **2000**, *45*, 35–43.
23. Wan Ngah, W.S.; Musa, A. Adsorption of humic acid onto chitin and chitosan. J. Appl. Polym. Sci. **1998**, *69* (12), 2305–2310.
24. Santana-Caslano, J.M.; González-Dávila, M. Characterization of the sorption and desorption of lindane to chitin in seawater using reversible and resistant components. Environ. Sci. Technol. **1992**, *26* (1), 90–95.
25. Thome, J.-P.; Patry, J.; Thys, I.; Weltrowski, M. New chitosan based PCB adsorbents: a synthesis. In: *Adv. Chitin Sci.* Domard, A., Jeuniaux, C., Muzzarelli, R.A.A., Roberts, G., Eds.; Jacques André Publisher: Lyon, France, 1996; Vol. I, 470–475.
26. McKay, G.; Blair, H.S.; Gardner, J.R. Adsorption of dyes on chitin. I. Equilibrium studies. J. Appl. Polym. Sci. **1982**, *27*, 3043–3057.
27. McKay, G.; Blair, H.S.; Gardner, J.R. Adsorption of dyestuffs onto chitin external mass transfer processes. J. Appl. Polym. Sci. **1982**, *27*, 4251–4261.
28. McKay, G.; Blair, H.S.; Gardner, J.R. The adsorption of dyes in chitin. III. Intraparticle diffusion processes. J. Appl. Polym. Sci. **1982**, *28*, 1767–1778.
29. Maghami, G.G.; Roberts, G.A.F. Studies on the adsorption of anionic dyes on chitosan. Makromol. Chem. **1988**, *189*, 2239–2243.
30. Yoshida, H.; Okamoto, A.; Kataoka, T. Adsorption of acid dye on cross-linked chitosan fibers, equilibria. Chem. Eng. Sci. **1993**, *48* (12), 2267–2272.
31. Stefancich, S.; Delben, F.; Muzzarelli, R.A.A. Interaction of soluble chitosans with dyes in water. I. Optical evidence. Carbohydr. Polym. **1994**, *24*, 17–23.
32. Delben, F.; Gabrielli, P.; Muzzarelli, R.A.A.; Stefancich, S. Interaction of soluble chitosans with dyes in water. II. Thermodynamic data. Carbohydr. Polym. **1994**, *24*, 25–30.

33. No, H.K.; Cho, Y.I.; Meyers, S.P. Dye binding capacity of commercial chitin products. J. Agric. Food Chem. **1996**, *44*, 1939–1942.
34. Juang, R.-S.; Tseng, R.-L.; Wu, F.-C.; Lee, S.-H. Adsorption behavior of reactive dyes from aqueous solutions on chitosan. J. Chem. Technol. Biotechnol. **1997**, *70* (4), 391–399.
35. Wu, F.-C.; Tseng, R.-L.; Juang, R.-S. Enhanced abilities of highly swollen chitosan beads for color removal and tyrosinase immobilization. J. Haz. Mater. **2001**, *81*, 167–177.
36. Weltrowski, M.; Patry, J.; Bourget, M. Reactive filter for textile dyes adsorption. In: *Adv. Chitin Sci.* Domard, A., Jeuniaux, C., Muzzarelli, R.A.A., Roberts, G., Eds.; Jacques André Publisher: Lyon, France, 1996; Vol. I, 462–469.
37. Low, K.S.; Lee, C.K. Quaternized rice husk as sorbents for reactive dyes. Bioresour. Technol. **1997**, *61*, 121–125.
38. McKay, G.; Ramprasad, G.; Mowli, P. Desorption and regeneration of dyes colours from low-cost materials. Water. Res. **1987**, *21* (3), 357–377.
39. Juang, R.-S.; Swei, S.L. Effect of dye nature on its adsorption from aqueous solutions onto activated carbon. Sep. Sci. Technol. **1996**, *31*, 2143–2158.
40. Sorlier, P.; Denuzière, A.; Viton, C.; Domard, A. Relation between the degree of acetylation and the electrostatic properties of chitin and chitosan. Biomacromolecules **2001**, *2* (3), 765–772.
41. Giles, C.H.; Hassan, A.S.A.; Subramanian, R.V.R. Adsorption at organic surfaces. IV—Adsorption of sulphonated azo dyes by chitin from aqueous solution. J. Soc. Dyers Colour **1952**, *74*, 682–688.
42. Lee, W.J.; Han, B.K.; Park, I.H.; Oh, H.I.; Jo, D.H. Effects of reaction temperature, time and particle size on the physicochemical properties of chitosans. Kor. J. Food Sci. Technol. **1995**, *27*, 997–1002.
43. Walker, G.M.; Weartherley, L.R. Adsorption of dyes from aqueous solution—The effect of adsorbant pore size distribution and dye aggregation. Chem. Eng. J. **2001**, *83*, 201–206.
44. Wu, F.-C.; Tseng, R.-L.; Juang, R.-S. Adsorption of dyes and phenols from water on the activated carbons prepared from corncob wastes. Environ. Technol. **2001**, *22*, 205–213.
45. Juang, R.-S.; Tseng, R.-L.; Wu, F.-C. Role of microporosity of activated carbons on their adsorption abilities for phenols and dyes. Adsorption **2001**, *7* (1), 65–72.
46. Guibal, E.; Milot, C.; Tobin, J.M. Metal anion sorption by chitosan beads: equilibrium and kinetic studies. Ind. Eng. Chem. Res. **1998**, *37* (4), 1454–1463.
47. EN ISO 7887.