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Screening of commercial sorbents for the removal of reactive dyes

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Abstract

Sorption filters could be a relatively simple treatment step to remove reactive dyes from textile wastewater. Activated carbon is already used in some treatment plants (loadings approx. 100 mg g^{-1}), and many non-regenerable products have been tested. This study aimed at identifying suitable sorbents for on-site regeneration. Zeolites, polymeric resins, ion exchangers and granulated ferric hydroxide (GEH) were tested with different reactive dyes (M 600–1500 g mol^{-1}). Zeolites and microporous resins were not suitable due to extremely low sorption capacities. The macroporous resins without functional groups showed moderate maximum loadings (100–400 μmol g^{-1} or 100–400 mg g^{-1}) but low affinity and were not suitable for large dyes (>1000 g mol^{-1}). loadings on anion exchangers were high but regeneration was difficult for the strong basic type (S6328a, Bayer). The weak basic type (MP62, Bayer) showed the most favorable profile: max. loadings of 200–1200 μmol g^{-1} (230–900 mg g^{-1}) and complete regeneration using alkaline methanol (10% water). With GEH moderate loadings of about 150 μmol g^{-1} were achieved. Catalytic oxidative regeneration of GEH is possible using H_2O_2. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ion exchange resins; Polymeric resins; Ferric hydroxide; Reactive dyes; Sorption; Textile wastewater

1. Introduction

The textile finishing industry has a high specific water demand of well over 100 liters per kg finished product. Hillenbrandt et al. [1] estimate 110–120 l kg^{-1} for the German textile industry and Kalliala and Talvenmaa [2] give similar figs. (100–500 l kg^{-1}) for Finland. Mixed textile wastewaters are complex media, containing a great variety of substances many of which are hard to remove. One problematic group are the reactive dyes—the largest single group of dyes used in the textile industry [3,4]. Being highly water soluble and practically non-biodegradable they are not degraded in municipal activated sludge treatment plants nor are they substantially removed via adsorption onto the biomass [5–7]. Removal of reactive dyes is necessary, however, on one hand, to prevent these recalcitrant compounds from release into the environment. On the other hand efficient and complete dye removal is necessary for water reuse in the industrial process.

Various types of reactive dyes are commercially available. Their common feature is a chemical reaction with the textile fiber to achieve a covalent dye-fiber bond. The reactive—or anchor—groups

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Nomenclature

A	absorption, cm^{-1}
c_0	original or feed concentration
c_{eq}	equilibrium concentration (dye), $\mu\text{mol l}^{-1}$
c_{res}	residual concentration
GEH	granulated iron hydroxide (β-FeOOH)
q	loading, mol g^{-1}
res	residual color, %
RR198	Reactive Red 198
RB5	Reactive Black 5
RB15	Reactive Blue 15
RO16	Reactive Orange 16
RR120	Reactive Red 120

vary as well as the chromophore. Dyes with two of the most commonly used anchors—the monochlorotriazine and the vinylsulfone group—were chosen for our study. All reactive dyes require alkaline conditions ($\text{pH} \geqslant 11$) for dyeing. However, in alkaline environment the formation of hydrolyzed, non-reactive oxy-dye competes with the dyeing reaction. (In this context hydrolysis means anchor inactivation, not bond cleavage with H_2O addition.) It is assumed that the predominant form found in wastewaters is the oxy-dye. However, all forms will be present to some extent [8,9].

Different methods can be used to treat reactive dye wastewaters. Aerobic biological treatment is ineffective [10], but most dyes are decolorized under anaerobic conditions [7,11]. However, further degradation of the metabolites—potentially toxic sulfonated aromatic amines—is not always possible [12,13]. Other approaches are oxidation, membrane separation, flocculation [10], or sorption processes.

Dye removal by sorption in fixed bed filters is a relatively simple method not involving complicated equipment. Activated carbon (AC) filters are already occasionally used, usually as one of the last steps in mixed wastewater treatment [14,15]. Moderate loadings of generally about 10–200 mg g^{-1} are achieved [5,16–20]. However, AC is relatively expensive and has to be regenerated off site with losses of about 10% in the thermal regeneration process. A great variety of other materials has been tested as sorbents for dyes, including reactive dyes. Most sorbents described in literature belong to one of the following groups: (a) organic waste materials such as eucalyptus bark (e.g. [21], many such materials were tested by Michelsen et al. [22]), (b) anion exchangers derived from quaternization of cellulose [23] or cellulose containing organic (waste) materials (e.g. [24]) or (c) clay materials [25]. Many of these sorbents display acceptable sorption capacities (typically around 20–400 mg g^{-1}). However, the sorbents are throw-away products that can only be used once and have to be disposed of afterwards. Virtually no literature about regenerable sorbents (other than AC) for reactive dye removal exists. The aim of this study was, therefore, to screen and investigate commercially available sorbents concerning their potential for removal of reactive dyes in fixed bed adsorption filters that can be regenerated on site.

A suitable sorbent has to meet the following criteria: (1) high affinity and capacity for target compounds, (2) regeneration must be possible, (3) safe and economically viable treatment/disposal of regenerate, (4) tolerance for a wide range of wastewater parameters, (5) usable for all or nearly all reactive dyes. The last point is important as dyers tend to use many different dyes in rapid succession.

Potential areas for practical application are final decolorization of pretreated mixed wastewater or dye removal from rinsing waters (after dyeing processes) for direct water recycling.

2. Materials and methods

2.1. Materials

Pure water was taken from a Millipore unit. Salts, acids and NaOH were of analytical quality (Fluka, Aldrich, Merck).

Reactive dyes were bought from Aldrich (RO16, RB15) or supplied by Ciba (RR120) and Dystar (RR198, RB5). Fig. 1 shows the five dyes presented in this article. In Table 1 their characteristics are summarized. The dyes are technical products with a pure dye content between 50 and 70% (see

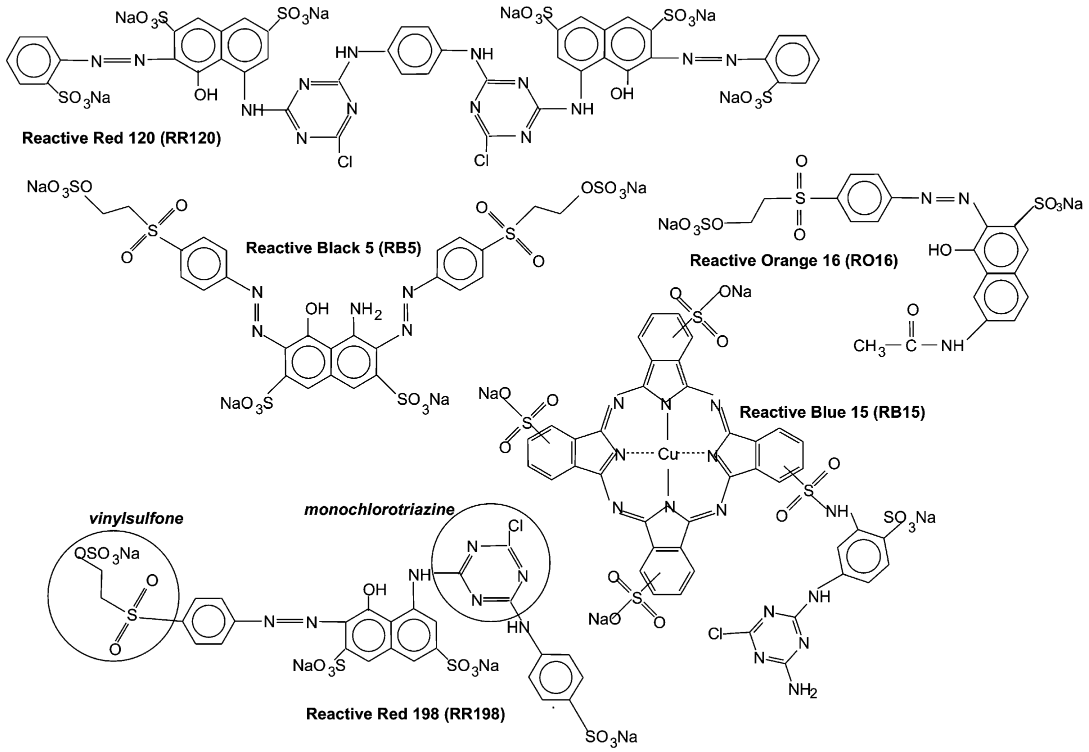

Fig. 1. Five dyes used in this study, unhydrolyzed, monochlorotriazine anchor and vinylsulfone anchor (non activated sulfato-ethyl-sulfone species) are highlighted.

Table 1
Characteristics of dyes used

Dye	Molar mass[a]	Percentage of pure dye	Anchor(s)	Chromophore
RR198	984.2	63%	Monochlorotriazine and vinylsulfone	Azo
RR120	1470	53%,	Monochlorotriazine	Azo
RB5	992	66%	Vinylsulfone	Azo
RB15	1283	35%	Monochlorotriazine	Phthalocyanine
RO16	617.5	44%	Vinylsulfone	Azo

[a] Molar mass of non-hydrolyzed dye.

Table 1). The pure dye content was calculated based on the organic N content of the mixtures determined by subtracting inorganic N (as determined by ion chromatography) from total N (as determined with a nitrogen analyser 1500, Fisons). Dyes were used "hydrolyzed" (see Introduction). For hydrolysis 5 g l^{-1} dye were dissolved in 0.1 M NaOH and heated to above 90 °C for 10 min. Hydrolysis transforms the monochlorotriazine group (see Fig. 1) into monohydroxytriazine and the sulfato-ethyl-sulfone anchor into hydroxy-ethyl-sulfone. Dye concentrations in experiments are generally given as mg l^{-1} of technical product ("tech."), whereas molar concentrations and loadings are calculated for presentation of equilibrium data.

The sorbents tested were three anion exchangers, S6328a, MP62 and P2, four polymeric resins without functional groups, OC1064, OC1066, P12 and EP63, two zeolites, DAY-P and DAZ-P, as well as a granulated iron hydroxide, GEH. Resins and anion exchangers were supplied by Bayer or Miontec, zeolites by Degussa and GEH by GEH-Wasserchemie. Characteristics of the sorbents are summarized in Table 2.

2.2. Equipment and analytics

Filtration was done with vacuum or pressure, using 0.2 μm cellulose acetate membrane filters (Sartorius, Machery and Nagel). The pH was measured using a ionode electrode (GAT) with a pH-meter (WTW). Absorption was determined with a UV–vis-spectrophotometer (Lambda 12, Perkin Elmer) at the maximum absorption wavelength of the respective dye in the visible spectrum. Residual color was calculated by comparing the absorption of the treated sample with a reference treated identically, but without sorbent:

$$\text{res} = A(\text{sample})/A(\text{reference}),$$
$$\text{where: res} = \text{residual color } (\%).$$

This was necessary because the molar extinction coefficients of the dyes change with pH and salt concentration. Residual concentrations were calculated by multiplying the residual color with the original concentration: $c_{\text{res}} = \text{res}{*}c_0$, where c_0 is the initial (or feed) concentration and c_{res} the residual concentration of pure dye. Pure dye concentrations were calculated based on the content of pure dye in the technical mixture (see above).

2.3. Experimental setup

Equilibrium sorption tests were performed by mixing concentrated dye solution, salt solution (when applied), diluting to a final volume of 100 ml and adding pulverized sorbent. The mixtures were stirred with magnetic stirrers at 20–25 °C for 72 h or more to reach equilibrium. The sorbent was then separated by filtration. This procedure was used to evaluate the influence of pH, (Na)sulfate, NaCl, and $CaCl_2$ and to collect isotherm data.

Regeneration and conditioning: regeneration agents were first screened via batch elution tests: Aliquots of loaded sorbent were mixed with equal volumes of different regenerant solutions and the resulting concentrations of desorbed dye or the calculated regeneration rates were compared. Efficiency of multiple regeneration and re-loading was tested in small laboratory filters (24 mm diameter, length 50 mm, filled with glass beads, and 1 g sorbent, wet, packed as a layer in between the beads). Two hundred millilitres of dye solution were used for loading (circular feed), then the sorbent was regenerated by cycling regenerant solution and washing with pure water (non-circular flow). For MP62 regeneration was followed by conditioning with HCl (0.1 M) for some tests. Conditioning was done in the same way as

Table 2
Characteristics of tested sorbents

Sorbent	Characterization	Pore size (nm)	Surface area ($m^2\,g^{-1}$)	Density per filter volume ($g\,l^{-1}$)
S6326a (Bayer)	Strong basic anion exchanger 0.8 eq l^{-1}	43	20–40	700
MP62 (Bayer)	Weak basic anion exchanger, 1.8 eq l^{-1}	35	36	600–700
P2	Weak basic anion exchanger, 0.19 eq l^{-1}	5	800	≈ 600–800
OC1064	Polystyrene, unfunctionalized	5–10	670	650–800
OC1066	Polystyrene, unfunctionalized	⩽ 5–10	700	650–800
P 12	Polystyrene, unfunctionalized	5–15	650	≈ 600–800
EP63	Polystyrene, unfunctionalized	0.5–10	1000–1400	
GEH	Granulated β-FeOOH	0.5–10	250–300	1220–1290
DAZ-P	Zeolithe	≈ 8		
DAY-P	Zeolithe	≈ 8		

regeneration. After regeneration (and conditioning) the next loading cycle was started.

3. Results and discussion

3.1. Screening

Sorbents were screened for their potential at different stages. In first tests for new sorbents sorption of one or two dyes was evaluated. Fig. 2 shows residual color and achieved loading (dye removed per dry matter of sorbent) for two zeolites, three polymeric resins, an anion exchanger and GEH (characteristics of all sorbents see Table 2).

Clearly, the zeolites, and EP63 remove virtually no dye and OC1066 only very little, whereas the other sorbents do achieve decoloration. In the case of OC1064 significant dye removal is obtained only in the presence of Ca. Zeolites and the microporous resin EP63 are evidently unsuitable and were excluded from further investigation. The micropores of EP63 are probably to small for the large dye molecules. Pore size also accounts for the difference between OC1064 and OC1066 which share the same matrix and only differ slightly in pore size. OC1064 has slightly larger pores and performs considerably better.

Further screenings were performed using a very small (RO16, $M = 618$ g mol^{-1}) and a very large dye (RB15, $M = 1283$ g mol^{-1}) in order to be able to account more clearly for pore size effects. Figs. 3 and 4 show the results of comparing the already mentioned materials OC1064, S6328a and GEH with one more unfunctionalized resin (P12) and two more anion exchangers (MP62 and P2). Note that loadings depend on residual concentration (as usually represented in isotherms) and that loading is limited by dye supplied in solution. However, maximum loading capacities can be estimated for some dye–sorbent combinations: Where no increase of loading is observed when increasing the dye/sorbent ratio by lowering the sorbent dose from 5 to 1 g l^{-1} the obtained loading can be considered the maximum possible loading.

The set of tests with RO16 (Fig. 3) shows the anion exchangers (and possibly OC1064) to have the highest removal efficiencies. The picture changes a little when regarding the sorption of the large phthalocyanine dye RB15 (Fig. 4). All loadings given in µmol g^{-1} are smaller, as a larger dye covers more surface area. Interestingly however, OC1064

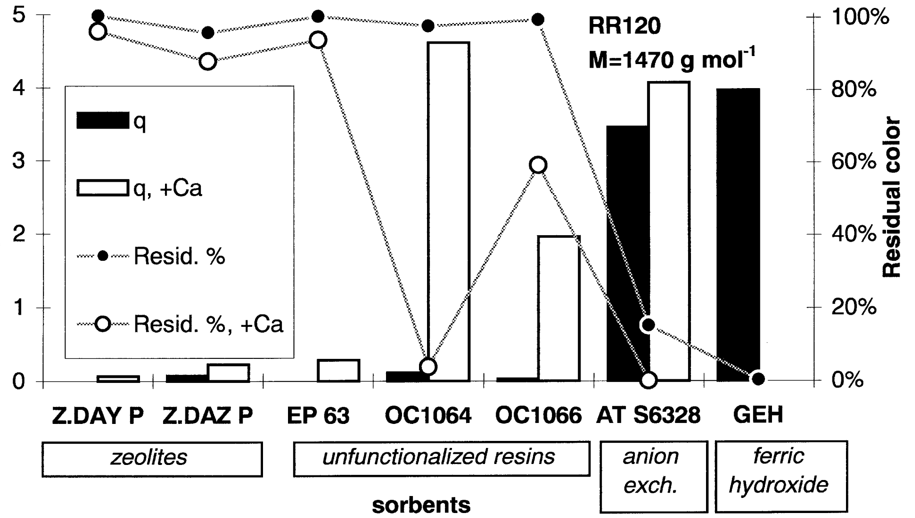

Fig. 2. Screening of sorbents I: obtained loading per dry matter of sorbent and residual color of model solution after treatment (batch experiment). Conditions: 50 mg l^{-1} of RR120 (technical product) dissolved in deinonized water, without and with added Ca (5 mmol l^{-1}). 10 g l^{-1} sorbent as supplied by manufacturer (zeolites: dry, other sorbents: wet). pH 7.

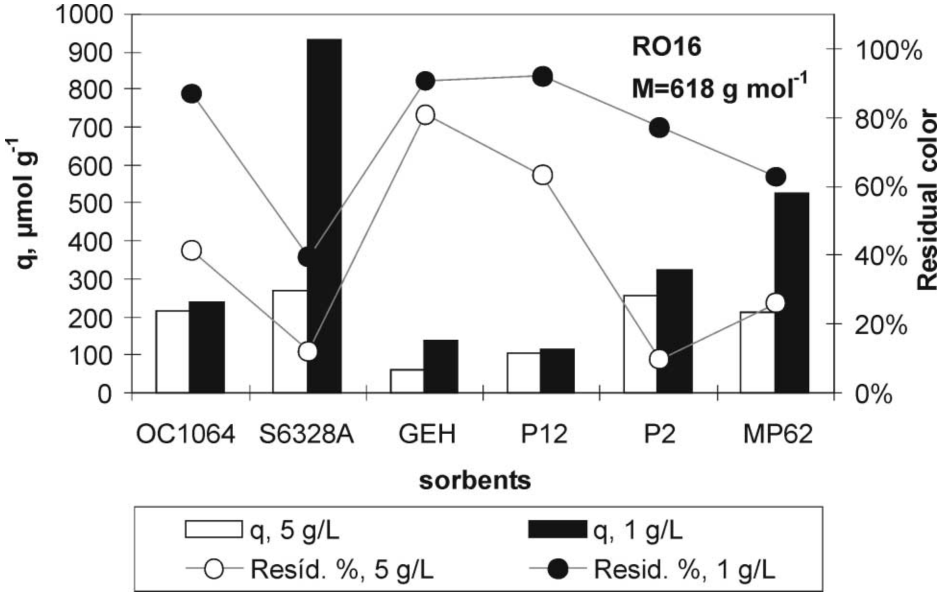

Fig. 3. Screening of sorbents II: obtained loading per dry matter of sorbent and residual color of model solution after treatment (batch experiment). Conditions: 1 and 5 g l^{-1} sorbent as supplied by manufacturer. 1 g l^{-1} of RO16 (technical product, hydrolyzed), 0.5 g l^{-1} for the tests with 5 g l^{-1} of GEH, P12, P2, MP62. pH 7.

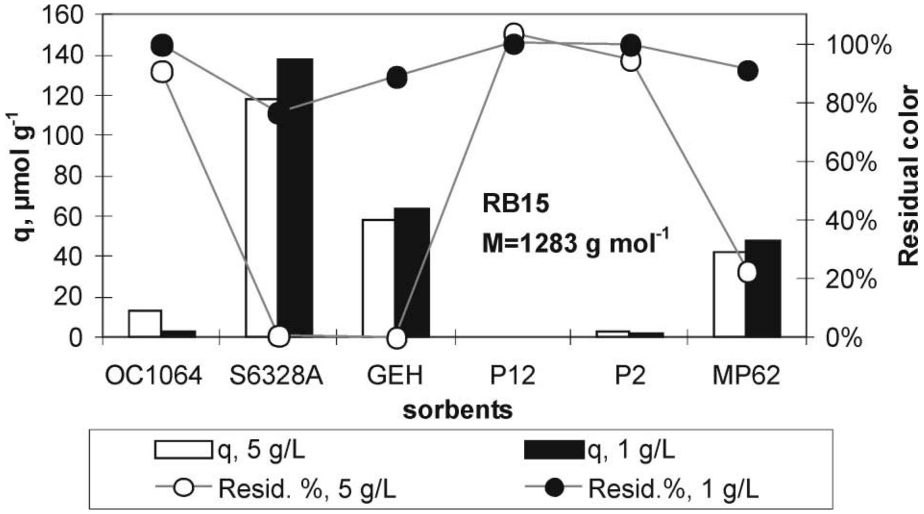

Fig. 4. Screening of sorbents III: obtained loading per dry matter of sorbent and residual color of model solution after treatment (batch experiment). Conditions: 1 and 5 g l^{-1} sorbent as supplied by manufacturer. 1 g l^{-1} of RB15 (technical product, hydrolyzed).

now shows practically no sorption whereas the GEH performs relatively well. Apparently OC1064 is very sensitive to dye size and GEH is not.

The screening tests leave the anion exchangers, GEH and possibly OC1064 as potentially effective sorbents that are further evaluated.

3.2. Equilibrium loadings and effects of wastewater parameters

Effects of wastewater parameters were investigated for the anion exchangers S6328a and MP62, for GEH and for OC1064.

Important parameters are pH, Na_2SO_4, NaCl, Na_2CO_3, Ca and temperature. The pH is relevant because the alkaline dyeing conditions can lead to alkaline wastewaters. NaCl and Na_2SO_4 are applied at high concentrations (up to 80 g l^{-1} in dye baths) to enhance bath exhaustion by lowering dye solubility. Na_2CO_3 on the other hand is used for pH adjustment (together with or as an alternative to NaOH) and as a pH buffer. The wastewater temperature can vary, especially when warm or hot washings steps are used. Ca is irrelevant for dyeing and pure rinsing (waste-)waters because softened water is generally used for these processes. Ca will be present in mixed wastewaters, though.

As shown in Fig. 5a the pH has practically no effect on dye sorption onto S6328a. The same is true for competing sulfate ions (Fig. 5b). A qualitative test for temperature influence showed no

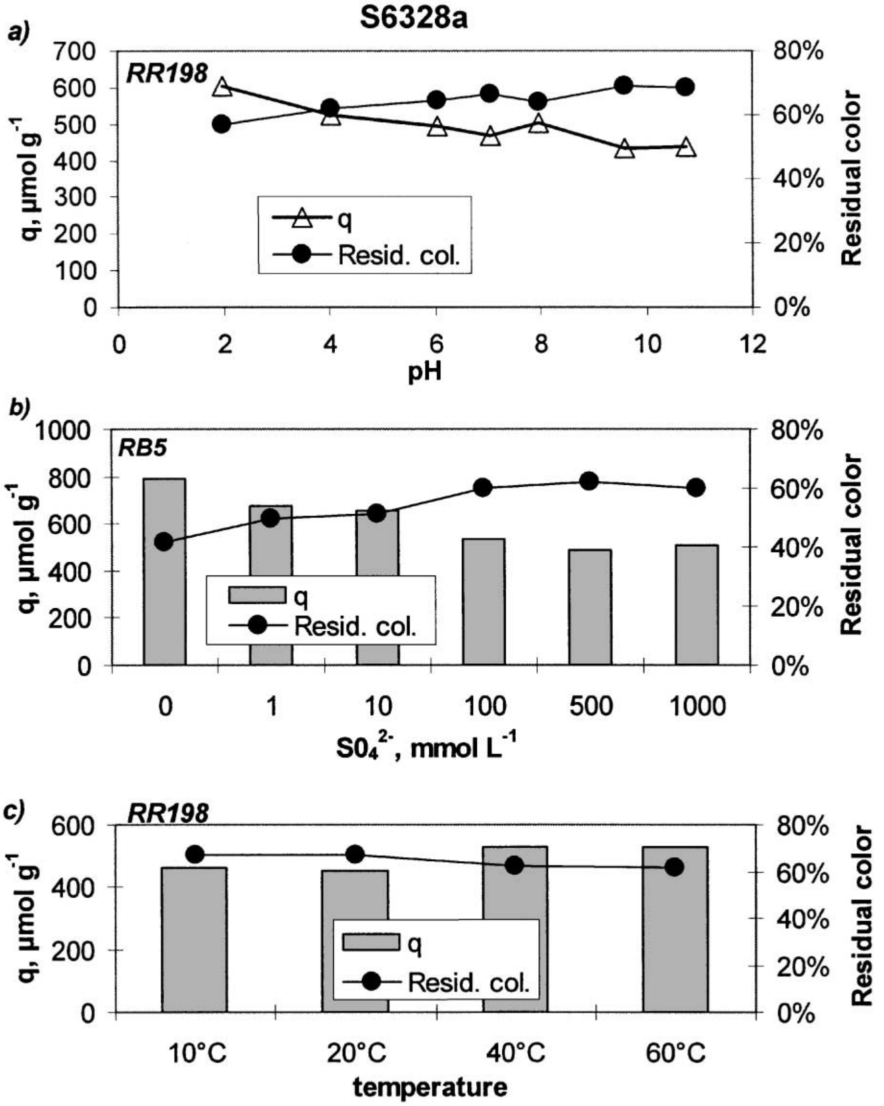

Fig. 5. Influence of (a) pH, (b) sulfate concentration, and (c) temperature on dye sorption onto S6328a. Conditions: (a) RR198 500 mg l^{-1} tech.; 0.5 g l^{-1} sorbent, wet; 0.2 mmol l^{-1} Ca, (b) RB5 200 mg l^{-1} tech.; 0.2 g l^{-1} sorbent, wet; 0.2 mmol l^{-1} Ca, pH 6–8, (c) RR198 500 mg l^{-1} tech.; 0.5 g l^{-1} sorbent, wet; 0.2 mmol l^{-1} Ca, pH 6.9–7.2.

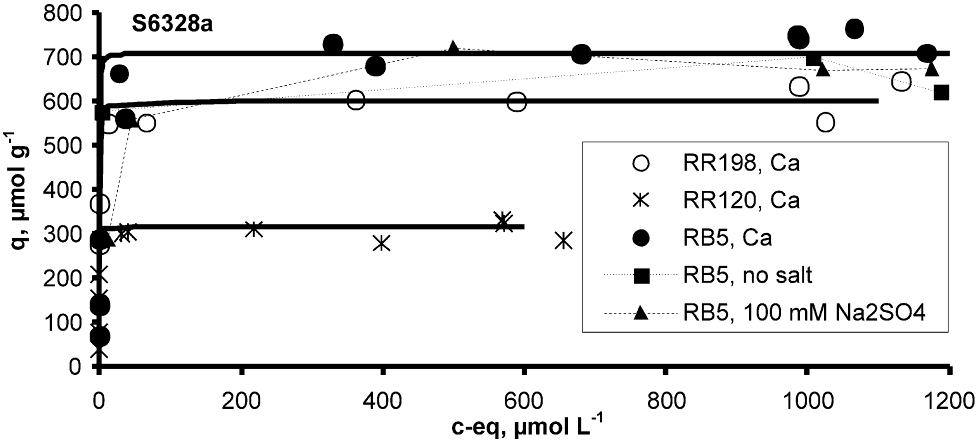

Fig. 6. Isotherms on S6328a. Effect of Ca and sulfate, different dyes. Conditions: pH approx. 7. RR198, RR120, RB5 0.2 mmol l^{-1} Ca, variation of c_0 (50–2000 mg l^{-1} tech., 1 g l^{-1} sorbent, wet) and *c* (sorbent) (2.5–10 g l^{-1}, c_0 1000 mg l^{-1} tech.). RB5 without salt and with sulfate, variation of *c* (sorbent) (0.5–10 g l^{-1}, c_0 2000 mg l^{-1} tech.).

Table 3
Percentage of theoretical anion exchange capacity used at maximum loading for S6328a and MP62 loaded with different dyes

Dye	SO_3^--groups	Loading S6328a (μmol g^{-1})	Used capacity[a] S6328a (%)	Loading MP62 (mmol g^{-1})	Used capacity[a] MP62 (%)
RR198	3	600	75%		
RB5	2	710	58%	1200	43%
RR120	6	315	75%	445	49%
RO16	2	⩾900	⩾75%	⩾567	⩾21%
RB15	4	⩾140	⩾23%	200	15%

[a] Total capacity: S6328a 2.4 meq g^{-1}; MP62 5.5 meq g^{-1}.

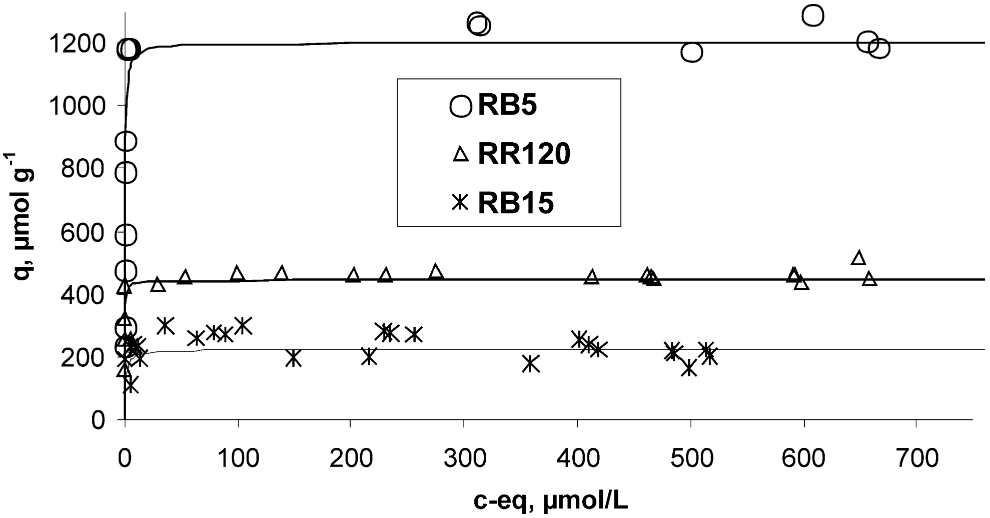

Fig. 7. Isotherms on MP62. RB5, RR120, and RB15. loadings on HCl-conditioned sorbent, calculated as dye per dry matter of unconditioned resin. Conditions: original pH 7, final pH 5. Variation of c_0 (25–2000 mg l^{-1} tech., 1 and 2 g l^{-1} sorbent, wet) and *c* (sorbent) (0.5–10 g l^{-1}, c_0 1000 and 200 mg l^{-1} tech.). No salts added.

detectable differences between batches treated at 10, 20, 40 and 60 °C (Fig. 5c). This was unexpected but a possible explanation is that the total enthalpy, consisting of the enthalpies of dye dehydration, Cl^- hydration, dye sorption and Cl^- desorption is not very large.

Fig. 6 shows isotherms for RB5 on S6328a under different conditions (with 2 mmol l^{-1} $CaCl_2$, without any added salts, and with 100 mmol l^{-1} sulfate) as well as equilibrium sorption data for 3 different dyes. It can be summarized that sorption of all tested dyes occurs with high affinity and

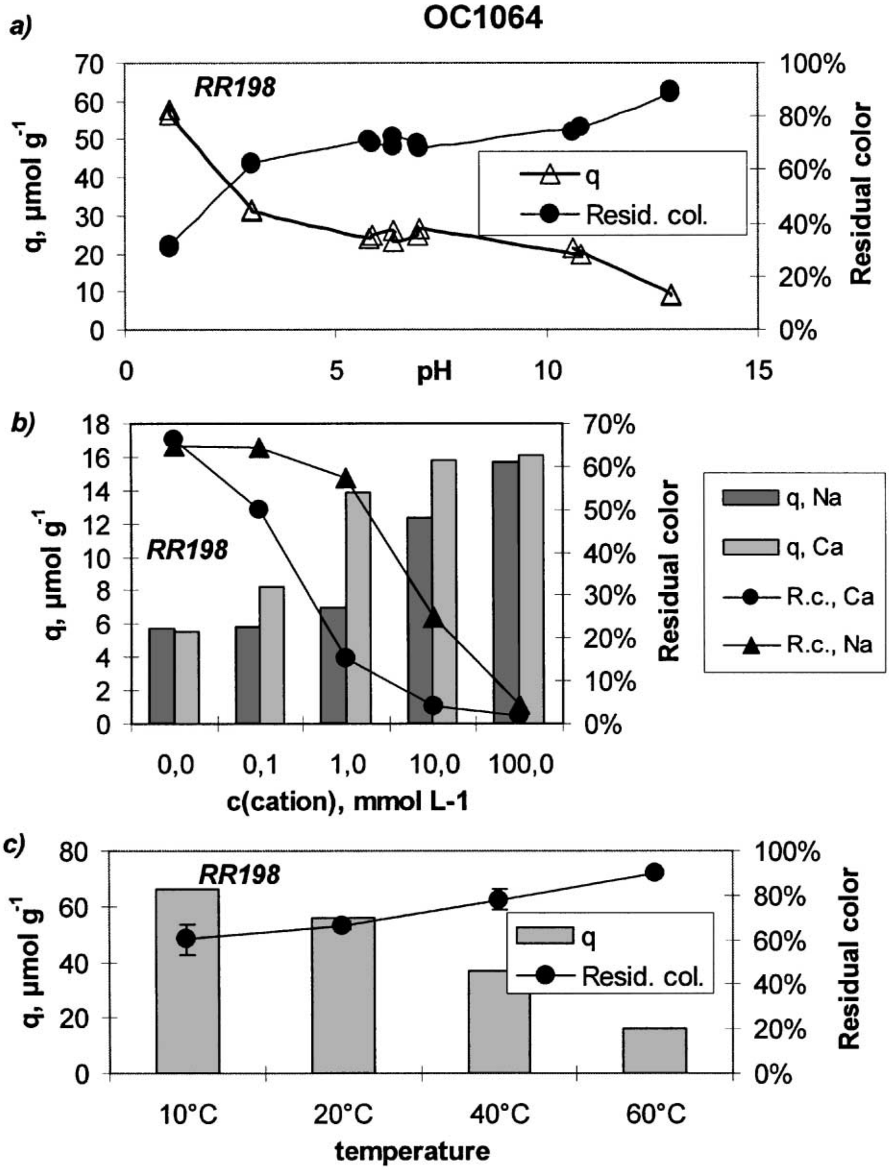

Fig. 8. Influence of (a) pH, (b) Na and Ca concentration, and (c) temperature on dye sorption onto OC1064. Conditions: (a) RR198 50 mg l^{-1} tech.; 0.1 g l^{-1} sorbent, wet; 0.2 mmol l^{-1} Ca, pH 6.5–7, (b) RR198 100 mg l^{-1} tech.; 10 g l^{-1} sorbent, wet; 0.2 mmol l^{-1} Ca, (c) RR198 50 mg l^{-1} tech.; 0.5 g l^{-1} sorbent, wet; 0.2 mmol l^{-1} Ca, pH 7–8.

capacity. Neither the absence of calcium nor the presence of sulfate (100 mmol l^{-1}) produce a significant change. RR120 shows the smallest molar loading, it is, however, the largest dye and also has more ionic groups. If loading is calculated as weight per weight there is no significant difference between all three dyes. In Table 3 maximum loadings and theoretical anion exchange capacity are compared. The fact that only 60–75% of the theoretical capacity are used in all cases suggests that size and not charge is the limiting factor. This is corroborated by the similar maximum loadings of RB5 and RR198 which have similar molar weights but different charges (−2 and −3, respectively, when hydrolyzed). The *sorption* characteristics of S6328a seem favorable for technical use.

Results from cyclic loading tests in small columns showed that MP62 does not adsorb dyes above pH 8. Dye removal is not detectably impaired in the presence of 100 mmol l^{-1} sulfate, though. Fig. 7 shows isotherms for 3 different dyes. Maximum loadings for other dyes were estimated from cyclic loading tests (see Regeneration) or screening tests (see above). Comparison of the maximum loadings and the theoretical ion exchange capacity is shown in Table 3. Again, it can be concluded that not all exchange sites can be occupied because maximum loading is limited by available surface.

Dye sorption onto OC1064 is not influenced by pH values between 4 and 10, but it improves below pH 4 and decreases above pH 10 (see Fig. 8a). This is presumably due to protonation of the organic sulfate groups of the dyes which increases their hydrophobicity and thus enhances their adsorbability. Adding salts also improves dye sorption as dye solubility decreases (see Fig. 8b). This is true for all tested salts (NaCl, Na_2SO_4, $CaCl_2$) but the effect is especially pronounced for calcium. At very low salt concentrations dye sorption is poor. As shown in Fig. 8c sorption decreases drastically with increasing temperature. Isotherms with different dyes, pH values and salt concentrations complete the picture (Fig. 9): In the presence of Ca (2 mmol l^{-1}) dye sorption is moderate (RR198) to good (RB5) for small to medium sized dyes (for sorption of RO16 see Fig. 3, above). large dyes such as RR120 and RB15 (see Fig. 4, above) are practically not removed. Without calcium in the solution the loading is considerably smaller—about half in the case of RB5. Thus the sorption characteristics of OC1064 are somewhat problematic for practical use. Dyes are not well removed from dilute, Ca-free waters which are found in rinsing steps after dyeing operations where softened water is generally used. Also, the sorbent is not suitable for the whole spectrum of dyes as large dyes sorb very poorly.

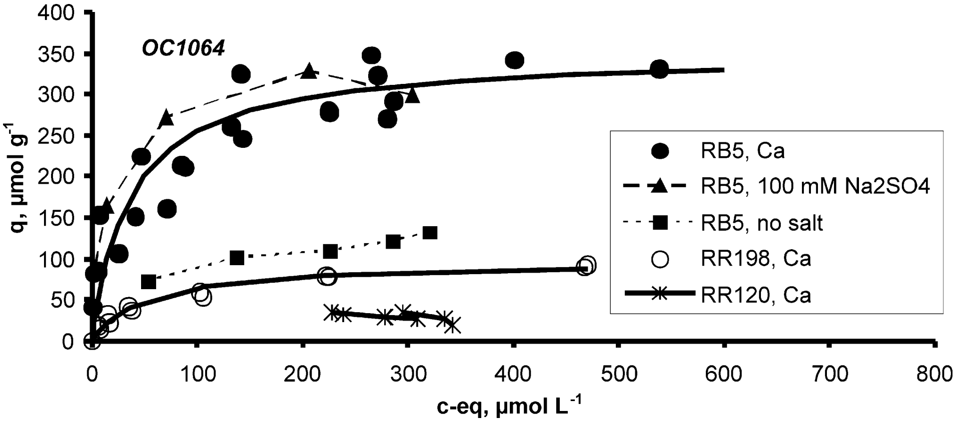

Fig. 9. Isotherms on OC1064. Effects of salts, different dyes. Conditions: pH approx. 7. RR198, RR120, RB5 0.2 mmol l^{-1} Ca, variation of c_0 (25–1000 mg l^{-1} tech., 1 g l^{-1} sorbent, wet) and *c* (sorbent) (0.5–10 g l^{-1}, c_0 1000 mg l^{-1} tech.). RB5 without salt and with sulfate, variation of *c* (sorbent) (0.25–10 g l^{-1}, c_0 500 mg l^{-1} tech.).

As shown in Fig. 10a dye sorption onto GEH is best at low pH values and starts increasing between pH 5 and 6. Up to about pH 8 reasonable loadings can be obtained. Sulfate has an adverse effect on dye sorption. As shown in Fig. 10b in a dye solution of 200 mg l^{-1} technical product (0.133 mmol l^{-1} pure dye) sulfate concentrations of 10 mmol l^{-1} and less already considerably diminish dye removal. As this effect is due to competition for sorption sites it of course depends on sulfate to dye ratio rather than absolute sulfate concentration. NaCl on the other hand has a positive effect on dye sorption. The effect of $CaCl_2$ is even stronger: loading in a batch with 1.25 g l^{-1} dye (tech.) and 4 g l^{-1} GEH (wet) increases by 20% when adding 5 mmol l^{-1} NaCl and by 70–90% when adding 2 mmol l^{-1} $CaCl_2$. Fig. 10c demonstrates a moderately strong negative effect of higher temperatures.

Equilibrium data for three dyes as well as the effects of high pH or high sulfate concentration

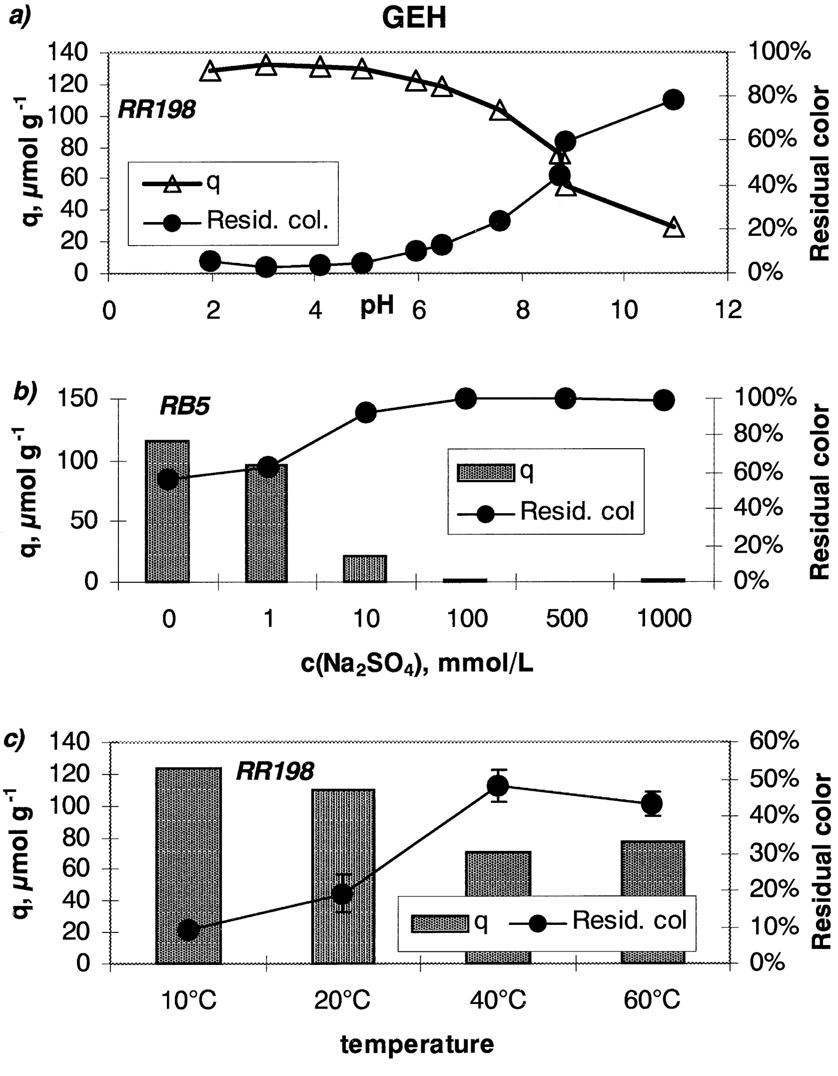

Fig. 10. Influence of (a) pH, (b) sulfate concentration, and (c) temperature on dye sorption onto GEH. Conditions: (a) RR198 50 mg l^{-1} tech.; 0.5 g l^{-1} sorbent, wet; 0.2 mmol l^{-1} Ca, (b) RB5 200 mg l^{-1} tech.; 1 g l^{-1} sorbent, wet; 0.2 mmol l^{-1} Ca, one sample without Ca nor sulfate, pH 6–8, (c) RR198 50 mg l^{-1} tech.; 0.5 g l^{-1} sorbent, wet; 0.2 mmol l^{-1} Ca, pH 7–8.

are presented in Fig. 11. For all three dyes similar, moderate molar loadings are achieved independent of the dye size. A pH of 9 considerably lowers the sorbent's capacity. The effect of sulfate is even stronger: Hardly any dye is removed when competing for sorption sites with sulfate at 100 mmol l^{-1}. Sorption onto GEH could be technically feasible for relatively dilute wastewaters with low sulfate content (carbonate and phosphate were not examined in detail but seem to have even stronger effects).

3.3. Regeneration and conditioning

S6328a cannot be regenerated using the more common methods, i.e. solutions of NaOH, NaCl or mixtures of these. However, most dyes can be desorbed with concentrated HCl or HCl–methanol mixtures. Unfortunately though, some relatively large and hydrophobic dyes such as RR120 precipitate at low pH values and thus cannot be removed from the sorbent. Fig. 12 shows several

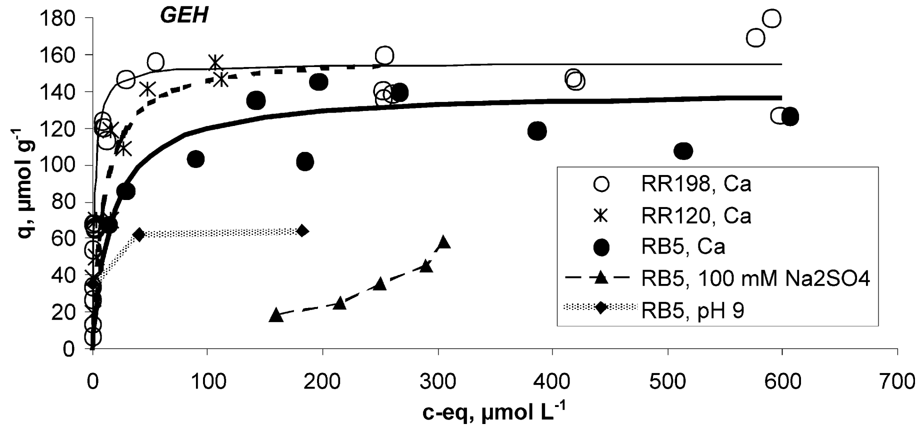

Fig. 11. Isotherms on GEH. Effects of salts, pH; different dyes. Conditions: pH approx. 7. RR198, RR120, RB5 0.2 mmol l^{-1} Ca, variation of c_0 (25–1000 mg l^{-1} tech., 1 g l^{-1} sorbent, wet) and *c* (sorbent) (0.5–10 g l^{-1}, c_0 1000 mg l^{-1} tech.). RB5 with sulfate and at pH 9 variation of *c* (sorbent) (1–20 g l^{-1}, c_0 500 mg l^{-1} tech.).

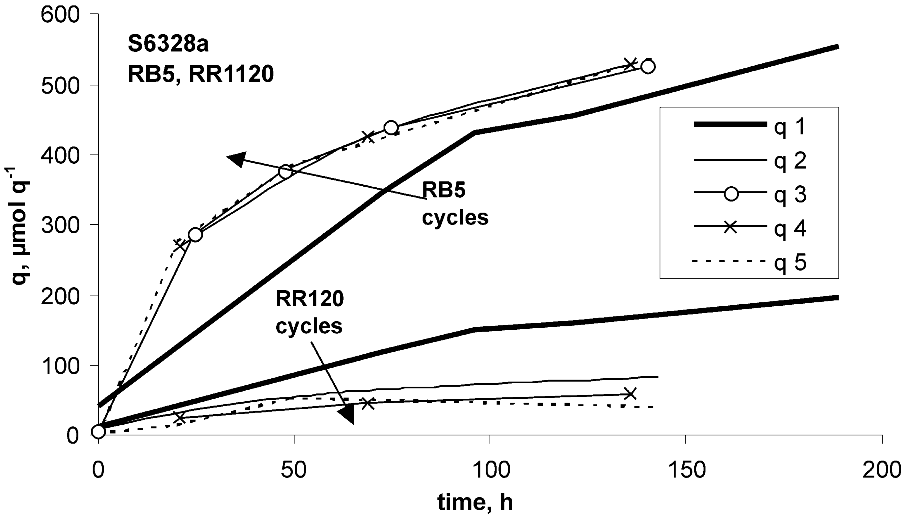

Fig. 12. Sequential loading and regeneration of S6328a in small filters (1 g sorbent, wet). HCl + methanol for regeneration. Original concentration 2 g l^{-1} tech., pH 7, volume 200 ml. Complete regeneration is achieved for RB5, not for RR120.

loading–regeneration cycles of a small laboratory filter with S6328a (cyclic feed) with RR120 and RB5 for comparison. With RB5 the original capacity is regained via desorption with HCl and methanol, whereas regeneration is clearly inefficient for RR120. Concerning practical usage regeneration of S6328a is problematic firstly because of the very aggressive regenerant and secondly because regeneration is not possible for the complete range of reactive dyes.

MP62 can be regenerated with NaOH solution and mixtures of NaOH with NaCl or methanol. Using NaCl alone does not work. Best results are achieved with the highest NaOH concentrations. Performance of MP62 is greatly improved by conditioning with HCl to protonate the tertiary amine groups. After regeneration with alkaline solution reconditioning is necessary. Fig. 13 shows loading regeneration cycles with and without conditioning (loadings are always calculated per dry matter of unconditioned sorbent). Tests with RB15 and RO16, and with sulfate added showed that loading and regeneration works with different dyes and is not impaired by competing sulfate anions (100 mmol l^{-1}). Regeneration of MP62 works well for model solutions. Optimization of regenerant composition and minimization of regenerant demand per sorbent as well as performance with original wastewaters still has to be investigated.

OC1064 can be regenerated with alkaline (0.05–0.1 M NaOH) water or methanol solution (with at least 5% water content). Fig. 14a shows regeneration efficiency of different methanol–water mixtures with no, 0.05 and 0.1 mol l^{-1} NaOH. The pure solvents (0 and 100% water) are clearly less potent than the mixtures, and alkaline solutions are more efficient than NaOH-free mixtures. There is no great difference, however, between the two different NaOH concentrations. Fig. 14b shows breakthrough curves in a very small filter for 3 loading–regeneration cycles. Clearly, the capacity does not change (as particle diffusion is slow, equilibrium loading will only be obtained after much longer running times). As for MP62, regeneration of OC1064 works well.

As shown elsewhere [26, 27] GEH can be regenerated using H_2O_2 ($\geqslant 1\%$ for satisfactory kinetics) without any loss in adsorption capacity. While oxidation of sorbed dyes already occurs at room temperature, a higher temperature of 40–50 °C is necessary for fast, efficient regeneration. Generally the possibility to oxidize sorbed dyes and to desorb formed oxidation products in one treatment step seems an elegant and promising solution. If the

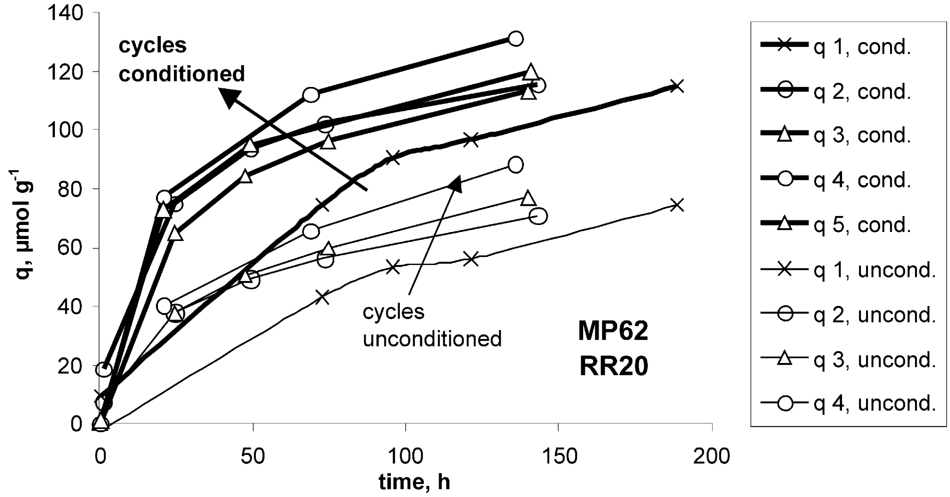

Fig. 13. Sequential loading and regeneration of MP62 in small filters (1 g sorbent, wet) with RR120, 200 ml, 1 g l^{-1} tech., pH 7 (final pH 5 for conditioned material). NaOH + methanol for regeneration. HCl for conditioning in one sequence. Complete regeneration is achieved in both cases.

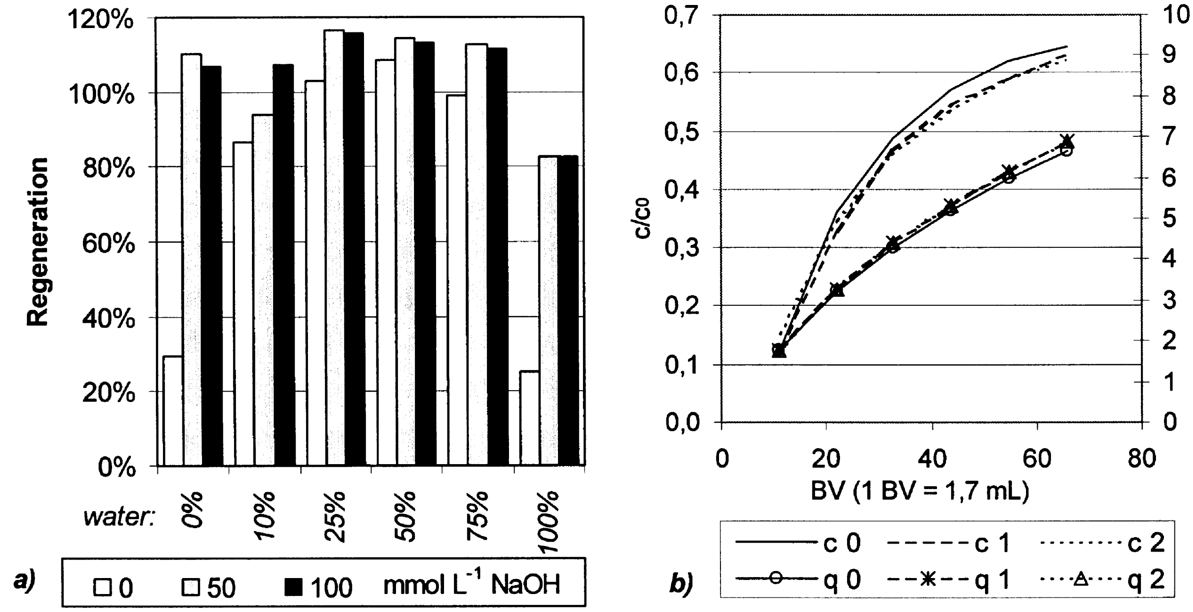

Fig. 14. Regeneration of OC1064 with different media (a) and sequential loading/regeneration using methanol with 50 mmol l^{-1} NaOH (b). Conditions: (a) 100 mg sorbent with $q = 65$ µmol g^{-1} of RR198, 50 ml of regenerant solution, 24 h elution time, (b) breakthrough curves of small filter (1 g sorbent, wet), feed concentration 200 mg l^{-1} tech. RR198.

biodegradability of the oxidation products is verified the regenerate can be discharged to the sewer and treated in municipal sewage treatment plants. Thus regenerate disposal could be achieved in an economically and ecologically sound way.

4. Conclusions

Zeolites and microporous resins are not suitable for reactive dye sorption. The pore sizes of these sorbents are too small for the rather large (approx. 600–1500 g mol^{-1}) dye molecules.

The strongly basic anion exchanger S6328a is not generally suitable for reactive dye removal. In spite of very good sorption characteristics it is not universally applicable because some dyes cannot be desorbed. Even where regeneration is possible, disposal of the strongly acidic regenerate solution is problematic.

The non-functionalized resin OC1064 has a relatively low capacity and affinity for the dyes in question. It almost completely fails to sorb large dyes (above approx. 1000 g mol^{-1}). Combined with its generally low capacity and affinity this means that the sorbent is not suitable for practical use.

The weakly basic anion exchange resin MP62, especially in the protonated form, has a very high capacity and affinity for reactive dyes. High concentrations of competing sulfate anions do not obstruct dye removal, however sorption only works at pH values below about 8. The sorbent can be reliably regenerated with a variety of alkaline regenerants. MP62 is a promising sorbent for reactive dye removal. Further tests to investigate filter kinetics and to optimize regeneration are necessary, though. Finally loading and regeneration of laboratory scale filters should be tested with original wastewater samples.

The granulated β-FeOOH GEH has a relatively low maximum capacity for reactive dyes but all tested dyes are removed with comparable efficiency, independent of molecular weight. When comparing loading per volume instead of loading per weight the capacity of GEH looks somewhat better since GEH has a density about twice the one of the other sorbents. Oxidative regeneration is an elegant method because sorbent regeneration and elimination of desorbed dyes is achieved in one step. Thus the material is an interesting sorbent for use in wastewaters with low concentrations of dyes and competing anions. Further investigation into product formation and biodegradability of oxidation products is necessary as well as testing regeneration of a greater variety of dyes.

Promising sorbents for use in textile wastewater treatment could be identified. However, the results achieved with model solutions have to be verified with original wastewaters and further research to quantify regenerant demand is necessary before a final evaluation of economical and ecological viability is possible.

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