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EVALUATION OF INORGANIC ADSORBENTS FOR THE REMOVAL OF PROBLEMATIC TEXTILE DYES AND PESTICIDES

S. D. Lambert, N. J. D. Graham, C. J. Sollars and G. D. Fowler

Department of Civil Engineering, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2BU, UK

ABSTRACT

This paper evaluates three inorganic adsorbents (activated bauxite, fullers earth and a synthetic clay), relative to activated carbon, for the removal of several representative contaminants of major concern and frequent occurrence in UK textile industry effluents; reactive dyes, pentachlorophenol and Propetamphos. The results indicate that, for the removal of reactive dyes, the synthetic clay was the most effective adsorbent over the pH range from pH 5.5 to pH 8.5 and temperature range from 20 to 40°C, although comparable dye removals were exhibited by activated carbon under neutral and alkaline conditions. Under acidic conditions activated bauxite was as effective as activated carbon. Fullers Earth was largely ineffective. With regard to the removal of pesticides activated carbon was highly effective, whereas the three inorganic adsorbents showed negligible removals. © 1997 IAWQ. Published by Elsevier Science Ltd.

KEYWORDS

Activated bauxite; activated carbon; adsorption; fullers earth; Macrosorb; pentachlorophenol; Propetamphos; reactive dyes; textile effluents.

INTRODUCTION

Water is consumed in large volumes by the textile industry and is an essential requirement of processes such as wool scouring, dyeing and mothproofing. However, the removal of contaminants from the effluents of such processes is problematic, with established technologies often unable to adequately reduce contaminant concentrations to desired and/or legislated levels. This has initiated a search for more effective, economic treatment techniques, of which adsorption processes appear to offer significant potential; they are inherently flexible processes that may be fully automated, incur significantly lower capital costs than, for example, ozone, membrane or biological processes and are suited to compact treatment plants, an essential requirement of textile processing utilities in the UK, many of which are situated in restricted inner city locations. The on-site treatment capability of adsorption processes would, in addition, allow process waters to be recycled, thereby reducing both effluent and process water charges. Inorganic adsorbents may also have a potential for *in situ* chemical regeneration. Without the requirement for thermal regeneration, therefore, inorganic adsorbents may have significantly reduced operational costs over adsorbents such as activated carbon.

This paper reports the results of bench-scale, batch adsorption trials with three inorganic adsorbents, activated bauxite, fullers earth and a synthetic clay material, and an activated carbon, for the removal of several contaminants of major concern and frequent occurrence in UK textile industry effluents; reactive dyes, the fungicide pentachlorophenol and organophosphorus sheep-dip chemicals.

MATERIALS AND METHODS

Materials

The three reactive dyes employed in this study were selected specifically because of the difficulty often experienced with their removal from textile effluents. They were comprised of Procion Turquoise H-A (C. I. Reactive Blue 71) and Procion Red H-E3B (C. I. Reactive Red 120), both supplied by Zeneca (Colours) Specialities, Blakely, UK, and Remazol Red RB (C. I. Reactive Red 198), supplied by Hoechst (UK) Ltd, Halifax, UK.

The two pesticides employed within this study were selected because of their frequent occurrence and high concentrations in textile effluents and consisted of the fungicide, pentachlorophenol, and the organophosphorus pesticide, Propetamphos. Samples of Propetamphos were supplied by Promochem Ltd, St. Albans, UK, and pentachlorophenol supplied by Greyhound Chromatography and Allied Chemicals, Birkenhead, UK. The purities of these samples were Propetamphos 99% and Pentachlorophenol 99%.

The three inorganic adsorbents were all received and used in a dry, powdered form and consisted of a gibbsitic bauxite (Alcan Chemicals Ltd, Gerrards Cross, UK), an activated fullers earth (Fulmont Premiere CP272, Laporte Industries Ltd, Widnes, UK) and a synthetic hydrotalcite clay (Macrosorb CT100, Crosfield, Warrington, UK). The powdered activated carbon used in this study (Picactif CNB100/EWN, Pica Carbons, Levallois Cédex, France) was selected following preliminary batch adsorption trials as the most effective of several carbon types for the adsorption of reactive dyes.

Methods

Based upon the results of thermogravimetric analyses, each of the inorganic adsorbents were initially calcined at 100°C intervals up to 800°C. The physical porous structures of each calcined phase were then characterised by gas adsorption techniques and their adsorbent properties examined by comparative batch dye adsorption tests. From these evaluations the optimal phases of each of the three inorganic adsorbents were selected for further study. These consisted of bauxite and Fullers earth calcined at 700°C and the synthetic clay used as received. All of these adsorbents, and the activated carbon, were thereafter chemically conditioned, as described by Lambert and Graham (1995a), to ensure clean, reproducible adsorbent surfaces representative of the bulk materials and their porous characteristics re-analysed. These are reported in Table 1.

Table 1. Adsorbent porous characteristics (STP)

Characteristic	Activated bauxite (Calcined at 700°C)	Fullers Earth (Calcined at 700°C)	Synthetic clay —	Pica carbon —
Specific surface area, BET (m^2/g)	93	257	87	1938
Meso-/macro-pore surface area, t-plot (m^2/g)	71	322	90	416
Meso-/macro-pore volume (mL/g)	0.25	0.53	0.34	0.65
Micro-pore volume, t-plot (mL/g)	0.10	0.00	0.00	0.75
BET constant, C	74	96	143	156
BET correlation coefficient	1.00	1.00	1.00	0.99

The comparative removal capacities of the adsorbents for the various contaminants were evaluated over a range of equilibrium pH (pH 5.5, 7.0, 8.5) and temperatures (20, 40°C) in a series of batch adsorption trials. In each trial, buffered (10^{-2}M $NaHCO_3$) solutions of individual contaminants were agitated for 48 hours with a range of adsorbent masses. It was established from preliminary trials that a contact time of 48 hours was sufficient to achieve 91, 92, 87 and 95% of the ultimate dye removal capacities of the bauxite, fullers earth, synthetic clay and activated carbon adsorbents, respectively. Initial concentrations of the dye and pesticide solutions contacted with the adsorbents were 20 mg/l and 150 µg/l, respectively. All dye working solutions were prepared by dissolving the appropriate mass of dye directly into solution as required. Working solutions of the pesticides were prepared by spiking with a known volume of 5 mg/l aqueous stock solutions.

Analyses

Residual dye concentrations were determined following pH adjustment by UV-/Vis-absorbance on an SP8-100 spectrophotometer (Pye-Unicam Ltd, Cambridge, UK). Following complete spectral scans, two discrete wavelengths, one in the visible region and the other in the UV region, corresponding to peak absorbances, were selected for the determination of each dye. These were 218 nm and 662 nm for Procion Turquoise H-A, 222 nm and 534 nm for Procion Red H-E3B and 282 nm and 514 nm for Remazol Red RB. In accordance with the Beer-Lambert law, all solutions exhibited linear UV-/Vis-absorbance values, at all wavelengths, with dye concentrations up to at least 100 mg/l.

All the pesticides were extracted from solution with dichloromethane, evaporated to incipient dryness, redissolved in a known volume of acetonitrile, and analysed by HPLC (Waters Chromatography, Watford, UK) using a Spherisorb ODS2 (5 µm, 46 x 250 mm) reverse phase column (Jones Chromatography, Hengoed, UK), an acetonitrile: water: acetic acid mobile phase and UV-absorbance detection. The composition and flow rate of the mobile phase and optimal wavelength for the separation and detection of each of the pesticides were determined empirically as stated in Table 2.

Table 2. Details of the HPLC pesticide analyses

Parameter	Pentachlorophenol	Propetamphos
Mobile phase composition (acetonitrile : water : acetic acid) (v/v)	70:29:1	85:14:1
Mobile phase flow rate (mL/min)	1	1
Detection wavelength (nm)	213	223
Injection volume (µL)	60	60
Retention time (min)	7.98	7.11

RESULTS

Removal of dyes

The results of the batch dye adsorption trials have been interpreted according to the Freundlich isotherm model, in which Ce is the equilibrium, residual contaminant concentration in solution, and qe is the contaminant concentration adsorbed per unit mass of adsorbent. Representative results are shown, as log versus log plots, in Figures 1 to 8. Figures 1 and 2 show the effects of pH on the dye removals of bauxite, synthetic clay and activated carbon. All the adsorbents are observed to be more effective with decreasing solution pH. However, whereas only a relatively minor effect is observed with pH on the removals achieved by the synthetic clay and activated carbon, the removals of bauxite are greatly influenced by the solution pH. Figures 3 to 5 show the comparative removals achieved by all the adsorbents for representative dyes with pH.

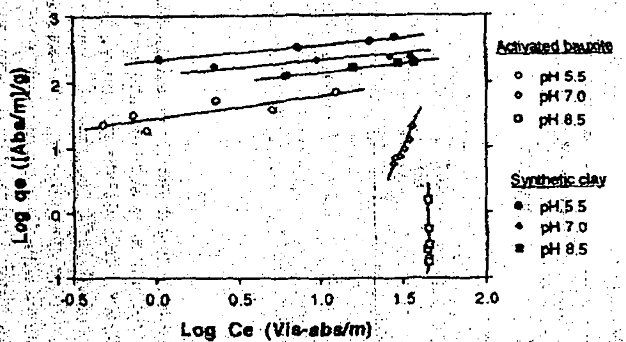

Fig. 1. Removals of Remazol Red by bauxite and synthetic clay with pH

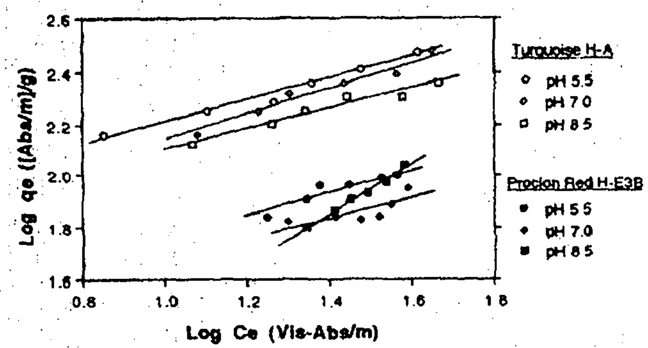

Fig. 2. Removals of Procion Red and Procion Turquoise by activated carbon with pH

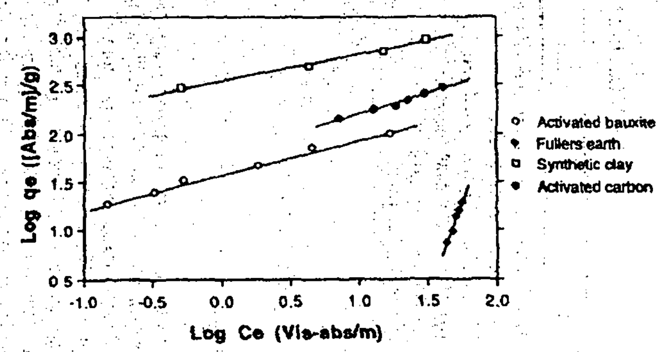

Fig. 3. Comparative removals of Procion Turquoise at pH 5.5

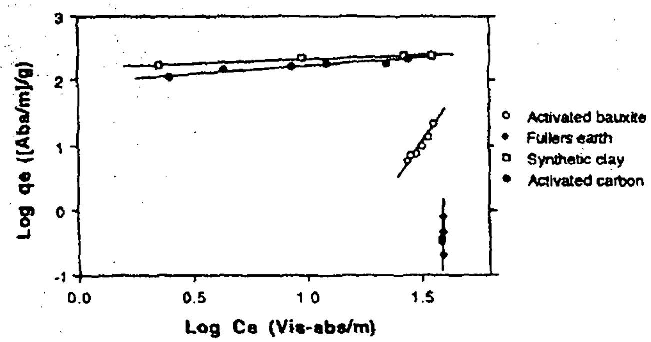

Fig. 4. Comparative removals of Remazol Red at pH 7.0

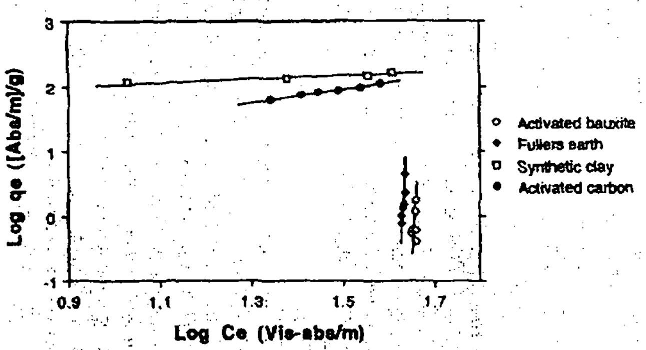

Fig. 5. Comparative removals of Procion Red at pH 8.5

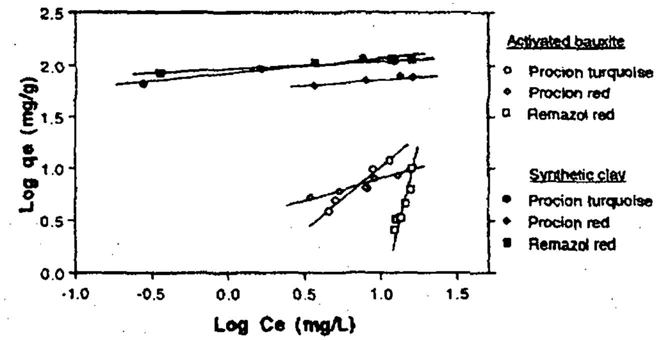

Fig. 6. Comparative dye removals by bauxite and synthetic clay at pH 7.0

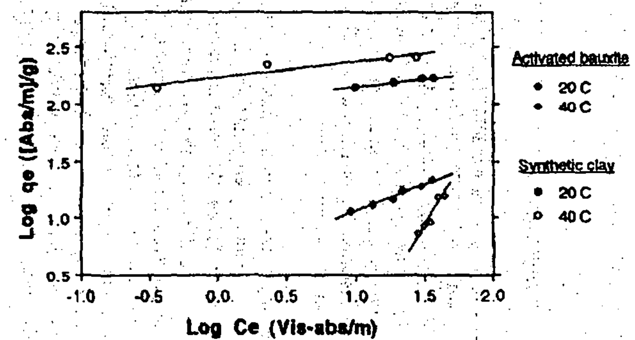

Fig. 7. Removals of Procion Red by bauxite and synthetic clay with temperature (pH 7.0)

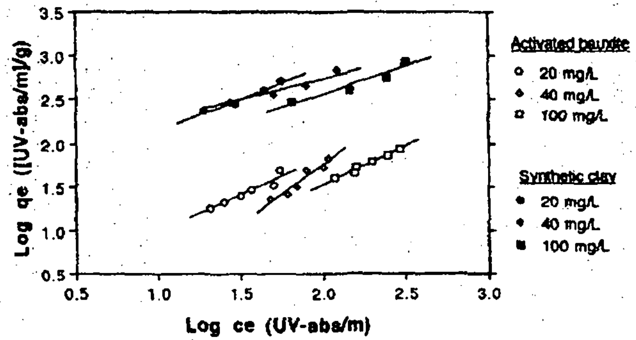

Fig. 8. Effect of Procion Red concentration on the removals by bauxite and synthetic clay (pH 7.0)

It is thus evident that the synthetic clay is the most effective adsorbent for the removal of reactive dyes at all solution pHs, although comparable removals are achieved by activated carbon under neutral and basic conditions. Under acidic conditions, bauxite is almost as effective for the removal of reactive dyes as activated carbon, but demonstrates negligible removals at pH 8.5. Fullers earth is shown to be ineffective at all the solution pHs investigated. Figure 6 shows the comparative removals of the three reactive dyes achieved by bauxite and synthetic clay. Due to the different magnitudes of UV-/Vis-absorbance exhibited by the three dyes, the results have been converted and expressed in terms of dye carbon masses (mg C). Some differences are observed in the removals of the various dyes by the adsorbents, although these were generally only relatively minor. Figure 7 shows the effects of temperature. Consequently, the capacity of bauxite for the adsorption of reactive dyes is shown to be better at lower temperatures. In contrast, the synthetic clay and activated carbon (not shown) are more effective for the adsorption of reactive dyes at higher temperatures. The effects of the initial dye concentration in solution were also investigated in Figure 8. It may thus be seen that for both bauxite and the synthetic clay, higher residual dye concentrations (Ce) remain at equivalent adsorbent loadings (qe) in solutions of higher initial dye concentrations. This means that, although not substantially different, the adsorbent capacities of both of the adsorbents are more effectively utilised in solutions of lower initial dye concentrations.

Removal of pesticides

The results of the Pentachlorophenol and Propetamphos batch adsorption trials are plotted, as above, according to the Freundlich isotherm model in Figures 9 to 11. Fullers earth demonstrated negligible pesticide removals (Figure 10) and, in addition to poor dye removals, was not fully evaluated.

Figure 9 shows the removal of Pentachlorophenol achieved by activated bauxite, synthetic clay and activated carbon. It is thus evident that the adsorption of Pentachlorophenol by both of the inorganic adsorbents is negligible and, by activated carbon, greater from solutions of lower pH. Similarly, Figure 10 shows that of all the adsorbents, only activated carbon is effective for the adsorption of Propetamphos with little influence of the solution pH on the adsorption characteristics observed. Figure 11 shows that greater Pentachlorophenol removals are achieved by activated carbon from solutions of lower temperatures. The adsorption of Propetamphos appears to be affected more by solution temperature which is greater at higher temperatures.

DISCUSSION

There are quite a number of advantages associated with the use of adsorbents for the on-site treatment of textile industry effluents. The most frequently applied adsorbent for the removal of organic contaminants in waters and wastewaters is currently activated carbon. However, activated carbon is not only an expensive material but, following exhaustion, incurs the high costs of thermal regeneration if it is to be re-used. The use of alternative cheaper adsorbents, therefore, or inorganic adsorbents with the potential to be regenerated chemically, is economically very attractive. This study has evaluated three such adsorbents, a synthetic clay, a Fullers earth and activated bauxite.

The synthetic clay evaluated in this study is actually presently used at several sites in the UK for the on-site treatment of textile industry effluents. At all of these sites, however, the clay is dosed as a slurry and, after rapidly raising the effluent pH and the addition of a coagulant aid, it is separated from the effluent and disposed of. Used in this way, the synthetic clay has been reported to be very effective, not only for the removal of reactive dyes, but also for some of the most frequently occurring pesticides (Cockett and Webb, 1995). The purchase cost of the synthetic clay is, however, comparable to that of activated carbon and a substantial economic benefit would, therefore, be achieved if the clay could be used as an adsorbent in a fixed bed, chemically regenerated and reused. However, whereas the synthetic clay, used simply as an adsorbent, has been demonstrated in this study to be very effective for the removal of reactive dyes, its capacity for the removal of pesticides was found to be negligible.

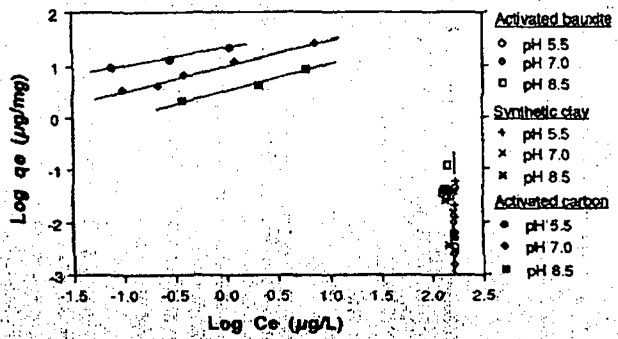

Fig. 9. Comparative removals of Pentachlorophenol

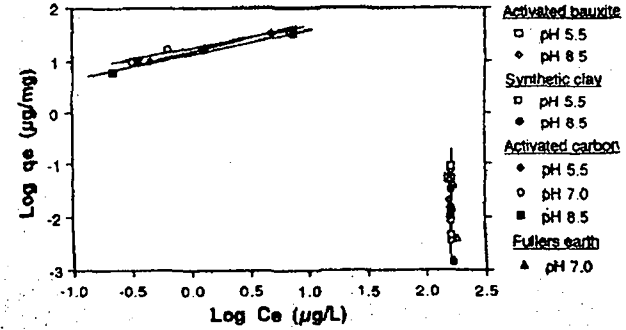

Fig. 10. Comparative removals of Propetamphos

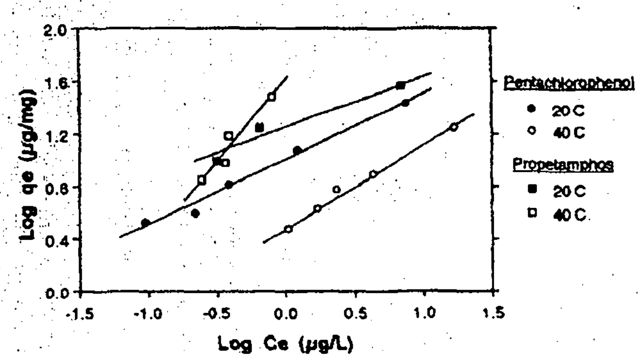

Fig. 11. Effect of temperature on pesticide removals by activated carbon (pH 7.0)

Fullers earth has also been shown previously to be very effective for the removal of textile dyes. It has been reported, for example, to be more effective than activated carbon for the adsorption of basic dyes and also very effective for the adsorption of acid dyes (McKay *et al.*, 1985). However, currently the most problematic dyes in the UK in terms of their removal from textile effluents are the reactive dyes for which Fullers earth has, in this study, demonstrated very little adsorption capability. Coupled with its negligible adsorption of the pesticides investigated Fullers earth would appear from this study to have little potential as an adsorbent for the on-site treatment of textile industry effluents.

Activated bauxite has not been extensively investigated as an adsorbent, although it has previously been shown to attain organic carbon removals from upland potable water sources approaching those of activated carbon subsequent to ozonation (Lambert and Graham, 1995b). This study has, in addition, shown activated bauxite to be very effective for the adsorption of reactive dyes, although its performance is greatly affected by the effluent pH. The poor adsorption of reactive dyes at high pH suggests, however, that dilute solutions of alkaline salts, such as NaOH or Na_2CO_3, might be very effective as chemical regenerants for bauxite. In addition to this potential for chemical regeneration, bauxite also has the advantage over both activated carbon and the synthetic clay of a very low comparative purchase cost, which might be used to offset some of its deficiencies as an adsorbent.

CONCLUSIONS

Inorganic adsorbents may have a significant potential for the on-site treatment of textile industry effluents containing reactive dyes. For example, the synthetic clay evaluated was more effective than activated carbon, over a range of solution pH and temperatures, for the removal of three problematic reactive dyes. Under acidic conditions bauxite similarly achieved dye removal efficiencies approaching those of activated carbon. Bauxite is, in addition, a very low cost material. Coupled with a potential for on-site chemical regeneration, the inorganic adsorbents may also have a major advantage over activated carbon for the removal of reactive dyes. However, for the removal of the most frequent and problematic pesticides from textile effluents, activated carbon was substantially better than the inorganic adsorbents, all of which were largely ineffective. Consequently, from the results of this study, a cost-effective solution for the on-site treatment of textile effluents containing both dyes and pesticides may be the combination of an inorganic adsorbent followed by activated carbon.

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