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Activated carbons developed from surplus sewage sludge for the removal of dyes from dilute aqueous solutions

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Abstract

Surplus biological sludge from wastewater treatment plants was pyrolysed at 700 °C in the presence of H_2SO_4. Sludge-based (SB) activated carbon (AC) was mainly mesoporous in nature, with a surface area of 253 m^2/g and an average pore diameter of 2.3 nm. Chemviron GW, an AC commercial reference, was mainly microporous with a surface area of 1026 m^2/g and an average diameter of 1.8 nm. SB AC outperformed the commercial product in the removal of three anionic dyes in solution (CI Acid Brown 283, CI Direct Red 89 and CI Direct Black 168). Chemviron GW performed best for Basic Red 46, which may be related to the relatively small steric size of the dye molecules compared with the size of micropores, and to the greater surface area of the commercial AC. For equilibrium pH values between 5 and 9, the adsorption capacity of SB AC for dyes was significantly modified due to the presence of ionisable surface functional groups while that of Chemviron GW, with a more hydrophobic surface, remained unaltered.

Keywords: Sewage sludge; Pyrolysis; Adsorption; Carbon adsorbent; Pore structure; Surface charge; pH_{ZPC}

1. Introduction

Activated carbon (AC) is a highly effective adsorbent that is extensively used for air and drinking water purification and is increasingly applied in industrial wastewater treatment. Despite the prolific use of this adsorbent, carbon adsorption remains an expensive treatment process [1]. The use of highly structured and robust activated carbons based on non-renewable and relatively expensive starting materials, such as coal, is unjustified in most pollution control applications. In recent years, this has prompted a growing research interest in the production of carbon-based adsorbents from a range of residues—mainly industrial or agricultural by-products. The production of activated carbon from residues may allow waste producers to offset their increasing waste disposal cost against the cost of carbon production, while saving non-renewable natural resources and producing a valuable product with potential applications in pollution control.

Petroleum wastes [2], waste newsprint paper [3] and a vast number of agricultural by-products including corn cob [4], flax shive [5], rice straw and hulls, sugarcane bagasse or pecan shells [6], among many others, have been successfully converted into activated carbons on a laboratory scale.

The process of carbonisation of sewage sludge, the by-product generated during wastewater treatment operations, has also been studied using different chemical agents and under various conditions, with the resulting solids having a surface area of 100–400 m^2/g [7–11]. The sludge-based (SB) AC obtained have been investigated for the adsorption of organic vapours [7] and more recently for other gaseous pollutants such as hydrogen sulphide [9–12] or nitrogen dioxide and sulphur dioxide [8]. With regard to liquid phase adsorption, sludge-based activated carbons have been evaluated for the removal of organics such as phenol, either by adsorption alone [12,13] or in a combined adsorption–biodegradation system [14].

Previous investigations showed that sludge-based activated carbons obtained in the presence of sulphuric acid possess relatively high adsorption capacity for aqueous species of large molecular weight [11]. Within this scope, the feasibility of employing ACs developed from sewage sludge by sulphuric acid activation for dye removal is explored in the present work and compared with a commercial activated carbon as a reference. The ability of SB AC for dye removal was evaluated using synthetic single solutions of four different dyes. Isothermal adsorption equilibrium data on SB AC were determined and modelled. The influence of

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the solution's pH on dye adsorption was also investigated to gain further insights into the mechanism governing the effectiveness of the SB AC.

2. Materials and methods

2.1. Materials

The powdered commercial activated carbon, Chemviron GW (Chemviron Carbon, UK) is produced by steam activation of bituminous coal. A sample of Chemviron GW for testing purposes was obtained from the local distributor. Chemviron GW was selected because of its high adsorption capacity for different molecular weight compounds such as phenol, iodine, methylene blue, and tannic acid when compared with other commercial products [11].

Four dyes of different types were supplied by Ciba-Geigy (Spain) in powdered form (Table 1). These were a cationic dye, Maxilon Red GRL-01 150 (CI Basic Red 46), and three anionic dyes, namely Lanacron Brown S-GR 150 (CI Acid Brown 283), Solofenil Scarlet BNL 200 (CI Direct Red 89) and Sella Black FS (CI Direct Black 168). Only some selected characteristics that may influence adsorption, such as the number of sulphonic groups ($–SO_3^-$) and azo groups (–N=N–) were made available by the supplier (Table 1). The molecular structures of Basic Red 46 [15] and Direct Black 168 [16] were found in the literature and are shown in Fig. 1. To determine the molecular dimension of these two dyes, full geometry optimisations without any symmetry constraints were carried out, using the AM1 semiempirical method [17] as implemented in AMPAC 6.55, a quantum chemistry program from Semichem [18].

Table 1
Properties of dyes

Colour index	Basic Red 46[a]	Acid Brown 283	Direct Red 89	Direct Black 168[a]
Type	Cationic	Anionic	Anionic	Anionic
Sulphonic groups	None	1	4	3
Azo groups	1	1	2	3
λ_{max}	530	322	496	614
pH range[b]	2–12	2–12	3–11	2–11

[a] See Fig. 1 and Table 2 for further details.

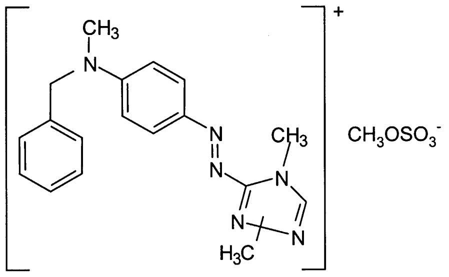
[b] The pH range of colour stability as measured by constant light absorption at λ_{max}.

2.2. Sludge-based activated carbons

The raw material used for activated carbon preparation was aerobically digested sludge from an urban wastewater treatment plant dewatered by centrifugation. The total dry solids (DS) and volatile solids (VS) were determined following standard procedures [19]. The raw sludge contains 17.6 g DS/100 g sludge, with 78% of VS (w/w). To manufacture the activated carbon, dewatered sludge was mixed with concentrated H_2SO_4 (17.5 M) (1:2, v/w) and dried in air at 105 °C. A sample of the dried material, weighing about 300 g, was then put into a crucible, heated in a fixed bed furnace at a rate of 15 °C/min to 700 °C in the presence of N_2 and held for 30 min. The samples were then allowed to cool to room temperature in an inert atmosphere. The product resulting from the activation step was ground and acid-washed using 50 ml of 3 M HCl per 100 g of product. The carbon product was then vacuum-filtered through Whatman 2 V filter paper and washed repeatedly with distilled water to remove all traces of the acid, i.e. until the pH of the rinse water was constant. The product was wet-screed through a 325-mesh sieve (particle diameter <45 μm) and dried at 110 °C overnight.

The purification step is needed to remove the activation agent and other inorganic residues. Essentially, vacant interstices in the carbon matrix are formed upon removal of the remaining activating agent by extensive post-pyrolysis washing, which also avoids any partial solubilisation and leaching of inorganic or organic matter from the pyrolysed

(a) Basic Red 46



(b) Direct Black 168

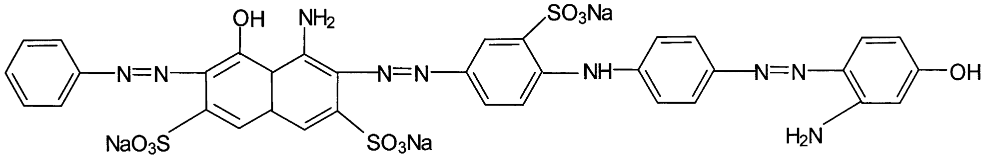


Fig. 1. Molecular structures of Basic Red 46 and Direct Black 168.

product. After purification, the conductivity of a 2 g SB AC/l suspension prepared in distilled water was around 95 µs, which is close to the values obtained with Chemviron GW (85 µs) under the same experimental conditions. Hence, it is likely that most of the leachable material is removed during the acid post-pyrolysis treatment.

2.3. Characterisation of activated carbons

The BET surface area of each activated carbon (S_{BET}) was obtained from N_2 adsorption isotherms at 77 K with a sorptiometer (Micromeritics ASAP 2000). From these data, the manufacturer's software also provided the total pore volume (V_{N_2}) by means of the Barrett–Joyner–Halenda theory, as well as the micropore ($V_{N_2}^{micro}$) and mesopore volume ($V_{N_2}^{meso}$) [20].

The iodine number (IN, mg/g), defined as the amount of iodine adsorbed per gram of activated carbon at an equilibrium concentration of 0.02N, was calculated from the adsorption isotherm as described in a previous work [11].

The pH value of carbon slurry was measured after stirring a 4 g/l mixture of activated carbon and distilled water for 2 h.

The pH of the zero point of charge (pH_{ZPC}) and surface charge density (σ) were measured by potentiometric acid–base titration of the activated carbon suspensions in 0.01 and 0.3 M NaCl. The titration procedure consisted of first degassing 0.1 l of a given electrolyte by bubbling N_2 until a constant pH of about 7 was reached. About 0.4 g of activated carbon were added and allowed to equilibrate for 1 h before titration was started. Two identical samples for each electrolyte concentration were prepared following this procedure, and titrated with 0.1 M HCl or 0.1 M NaOH. An equal volume of the electrolyte in the absence of activated carbon was also titrated with NaOH and HCl to obtain the blank curve at each electrolyte concentration. The titrations were performed by adding 0.5 ml of titrant, with 5 min contact allowed before the equilibrium pH was recorded. During titration, the solutions were magnetically stirred, and purified N_2 was bubbled preventing any interaction with CO_2.

The pH value at which the surface of an activated carbon has a neutral charge, i.e. the pH of zero point charge (pH_{ZPC}) was determined by the intersection of the titration curves at different electrolyte concentrations. The relative surface charge density (σ_0, in C/g) was determined from the difference between surface titration curves and the blank curves as follows:

$$\sigma_0 = \frac{\Delta v M F}{[\mathrm{AC}] V}$$

where Δv is the difference between the titrant volumes used for the activated carbon slurry and the blank at given pH values (l), M is molarity of the titrant (mol/l), F is the Faraday's constant (96,490 C/mol), [AC] is the activated carbon concentration (g/l), and V is the volume of electrolyte (l).

The surface charge density (σ, C/g) was then calculated so as to make $\sigma = 0$ C/g at pH = pH_{ZPC} and therefore was calculated for any given pH as

$$\sigma = \sigma_0 - \sigma_0^{pH_{ZPC}}$$

with the resultant plot giving the absolute surface charge (σ) versus pH.

2.4. Equilibrium batch dye adsorption experiments

To determine the isothermal adsorption capacity, a series of 250 ml Erlenmeyer's solutions of consecutively increasing initial dye concentration ranging from 30 to 250 mg/l were prepared. A constant volume of 0.1 l of dye solution and 0.4 g of activated carbon were used. Previous experiments have shown that the amount of dye adsorbed sharply increased with time and reached their plateau values within 1 h. Based on this result, the isothermal (20 °C) adsorption capacity determined after 2 h of contact. The pH was then measured and the activated carbon separated by vacuum filtration through a Whatman 2 V filter. The first part of the dye solution to come through was discarded to eliminate the effects of any adsorption onto the glass fibre filter. Each experiment was duplicated under identical conditions. The dye concentration was analysed using a Hitachi UV-2000 spectrophotometer by measuring the optical density on the respective maximum absorbance wavelengths (λ_{max}, Table 1). Calibration curves were established prior to the analysis. Dilutions were performed where necessary to bring the analyte solutions within the calibration range.

A second set of experiments was carried out to ascertain the effect of pH on the adsorption of dyes on both the sludge-based and the commercial activated carbon using a constant initial dye concentration of 100 mg/l. Prior to adsorption experiments, the colour stability of each dye under different pH conditions was investigated by modifying the pH of the initial dye solution with HNO_3 (1 M) or NaOH (1 M). The colour was considered stable if no change in its light absorption at λ_{max} was observed. The pH range of colour stability is shown in Table 1. For the adsorption experiments, 0.4 g of activated carbon were added to 100 ml of the initial dye solution and the pH adjusted to the desired value with HNO_3 (1 M) or NaOH (1 M). After 2 h of contact, the equilibrium pH was recorded (pH_{eq}), and the dye concentration was determined as previously described.

3. Results and discussion

Surplus biological sludge from wastewater treatment plants was investigated as a raw material for the production of an adsorbent. The average DS content was 17.6% (w/w), of which about 78% of DS was organic matter. As would be expected for a digested municipal sludge, the elemental carbon content is high, around 58% (w/w) of the organic fraction (Table 2) and significant amounts of N are found (9% (w/w) of the organic fraction). The inorganic residue

Table 2
Selected chemical properties of Basic Red 46 and Direct Black 168

Chemical properties[a]	Basic Red 46	Direct Black 168
Molecular weight (g/mol)	322	734
Width (nm)	1.3	2.0
Depth (nm)	0.74	0.11
Thickness (nm)	0.63	0.57

[a] Associated counter ions are not included.

Table 4
Characteristics of the porous structure of sludge-based and the commercial activated carbon

	Activated carbon	
	Sludge-based	Chemviron GW
Nitrogen adsorption		
S_{BET} (m^2/g)	253	1026
S_{micro} (m^2/g)	90	630
Average pore diameter (nm)	2.3	1.8
V_{N_2} (cm^3/g)	0.20	0.49
$V_{N_2}^{micro}$	0.08	0.39
$V_{N_2}^{meso}$	0.12	0.10
Iodine adsorption		
IN (mg I_2/g)	575	810
V_{I_2} (cm^3/g)	0.15	0.22
V_{I_2}/V_{N_2}	0.75	0.44

after heating the thermally dried sludge at 500 °C in air is 22% of the DS content. This ash would be expected to consist of inorganic oxides such as SiO_2, Fe_2O_3, and CaO [21]. The surface area of the dried sludge as measured by nitrogen adsorption is about 3 m^2/g, in agreement with previously published results for the same type of material and treatment [12]. Although the use of dried sludge as an adsorbent has been suggested in the literature [22], a partial solubilisation when brought into contact with water was detected, releasing organic and/or inorganic compounds, which impairs its application as an adsorbent. Previous investigations have demonstrated that a stable solid with good adsorption capacity is obtained if sludge is mixed with H_2SO_4 and pyrolysed at 700 °C for 30 min with an average product yield of 46% [11]. The activated carbon obtained under these experimental conditions was characterised and its application to the removal of dyes in solution investigated.

3.1. Characteristics of the sludge-based activated carbon

The characteristics of the activated carbon resulting from the pyrolysis of surplus sludge in the presence of H_2SO_4 followed by acid washing are shown in Tables 3 and 4.

The S_{BET} value reported in Table 4 for sludge-based activated carbon shows that the evolution of organic matter during pyrolysis results in a clear improvement on the surface area of the SB adsorbent, from 3 m^2/g measured for the raw dried sludge, to a value of around 253 m^2/g for the high-temperature treated char. Through pyrolysis, the resulting product is enriched in carbon as shown by the ultimate analysis of the organic fraction in Table 3. The increases of C/H and C/O molar ratios of the SB AC with respect to the raw dried sludge are indicative of a dehydrogenative polymerisation and dehydrative polycondensation reactions during acid and heat treatment, with significant loss of aliphatic hydrogen through olygomerisation and of oxygen-containing structures through polycondensation reactions. The increase in *S* content may be attributed to the formation of alkyl hydrogen sulphates, since unreacted sulphuric acid is removed by extensive washing after pyrolysis [23]. Despite being subjected to an intensive post-pyrolysis acid wash, the resulting AC has a substantial ash content (39.2%, w/w), due to the high ash content of the raw material, i.e. dried sludge (22%, w/w), and the partial volatilisation of organic matter during the course of pyrolysis.

SB AC differs significantly from Chemviron GW, the commercial product chosen for comparison, in both its porous structure and its chemical composition. As shown in Table 4, SB AC has a considerably lower S_{BET} than the commercial activated carbon Chemviron GW as determined by N_2 adsorption. The lower S_{BET} of the SB AC is related to the little microporosity present, i.e. low presence of pores of diameter (d) <2 nm, while it shows a well-developed mesoporous ($2\,nm < d < 50\,nm$) structure with an associated $V_{N_2}^{meso}$ similar to that of the commercial product.

As an alternative method to gain further knowledge on SB AC porous structure, iodine (I_2) adsorption from liquid phase was performed. The adsorption of aqueous I_2 is considered a simple and quick test for evaluating the surface area of activated carbons associated with pores with $d >$ 1 nm [24]. It is assumed that I_2 at an equilibrium concentration of 0.02N is adsorbed into the carbon in the form of a monolayer and the amount adsorbed at this equilibrium

Table 3
Chemical composition of the sludge used as a raw material, the sludge-based activated carbon (AC) and the commercial Chemviron GW AC

Sample	pH	Ash (wt.%)	Ultimate analysis (wt.%)					Molar ratio		
			C	H	N	S	O[a]	C/H	C/N	C/O
Dried sludge	–	22.0	57.7	8.5	9.3	0.5	24.0	0.57	7.24	3.20
Sludge-based AC	4.5	39.2	69.7	2.1	10.2	8.2	9.7	2.76	7.97	9.58
Chemviron GW AC	7	3.7	89.8	0.8	–	–	9.4	9.35	0	12.7

[a] By difference.

concentration called the iodine number (mg I_2/g AC). Multiplication of IN (Table 4) by the liquid molar volume of I_2, 68 mol/cm^3, would give the maximum volume accessible (i.e. V_{I_2}, Table 4) for the adsorption of I_2 from the liquid phase [25]. The value of V_{I_2} for the SB and the commercial AC derived from the liquid phase adsorption was found to be smaller than the total pore volume determined by N_2 adsorption, indicating that, for both AC, part of the micropores that make up the structure are not accessible to the iodine molecule in aqueous solution. However, the ratio V_{I_2}/V_{N_2} for SB AC indicates that an important fraction (0.75) of the total porosity that makes up its structure is accessible to the iodine molecule in aqueous solution, while for the commercial AC it is only 0.44, i.e. the proportion of very fine pores ($d < 1$ nm) inaccessible to the iodine molecule is highly significant.

The pH of the aqueous slurry of the SB AC is 4.5 (Table 3) and can be classified as an acid-type L AC, since it exhibits a pH value lower than that of distilled water (pH = 6.5) [26], while for Chemviron GW the pH was around neutral (pH = 7). The low pH value of the SB AC slurry arises from the presence of acidic surface functional groups, mainly carboxyl groups (R–COOH) and phenolic groups (R–OH), while the surface of Chemviron GW was found to be more hydrophobic in nature, with no functional groups detected by titration. The presence of ionisable functional groups may render the surface of activated carbon positively or negatively charged as a function of solution pH. The surface charge density (σ, C/g), defined by the net uptake of protons and determined from the potentiometric titrations of SB AC and Chemviron GW as a function of pH is shown in Fig. 2. The curve corresponding to SB AC clearly reflects that σ is strongly dependent on solution pH, changing from positive to negative for pH values above the pH of zero point charge, i.e. $\mathrm{pH_{ZPC}} = 4$. The negative σ arises from the deprotonation of acidic functional groups of the carboxyl and phenol type on the surface of SB AC. For Chemviron GW, σ (Fig. 2) varies from positive at pH <7.2 to negative at higher pH values, although σ is only significantly modified at extreme pH values, i.e. for pH <4.5 and pH >10.

3.2. Isothermal adsorption capacity of sludge-based activated carbon for dyes

The produced SB AC and the commercial AC were tested for their adsorption efficiency for different types of dyes (Table 1). To determine the adsorption isotherms, the initial dye concentration ranged from 30 to 250 mg dye/l, which falls within the range of reported concentrations of dyes in dyehouse effluents [27]. The adsorption process was studied without any control over the pH of the aqueous phase. The pH values of the dye-activated carbon slurries after adsorption were around 7.4 for GW, while equilibrium pH values for the SB AC were acidic (pH around 4.2), which are close to the $\mathrm{pH_{ZPC}}$ of each adsorbent (Fig. 2).

The adsorption isotherms obtained under these experimental conditions for the four dyes on both the SB and commercial ACs are shown in Fig. 3, where the amount of dye adsorbed (q, mg dye/g AC) is plotted against the dye equilibrium concentration (C_{eq}, mg/l). The isotherms for the adsorption of dyes on the commercial activated carbon Chemviron GW reflect a trend of levelling out at higher adsorbate concentrations, corresponding to the completion of a monolayer in the experimental concentration range. The shapes of the adsorption isotherms on SB AC are different. For the adsorption of dyes on SB AC, q varies more linearly as a function of equilibrium concentration with saturation only clearly observed for Acid Brown 283.

The equilibrium concentrations in the adsorption experiments were treated by the classical Langmuir equation:

$$q = \frac{Q_{\mathrm{m}} b C_{\mathrm{eq}}}{1 + b C_{\mathrm{eq}}}$$

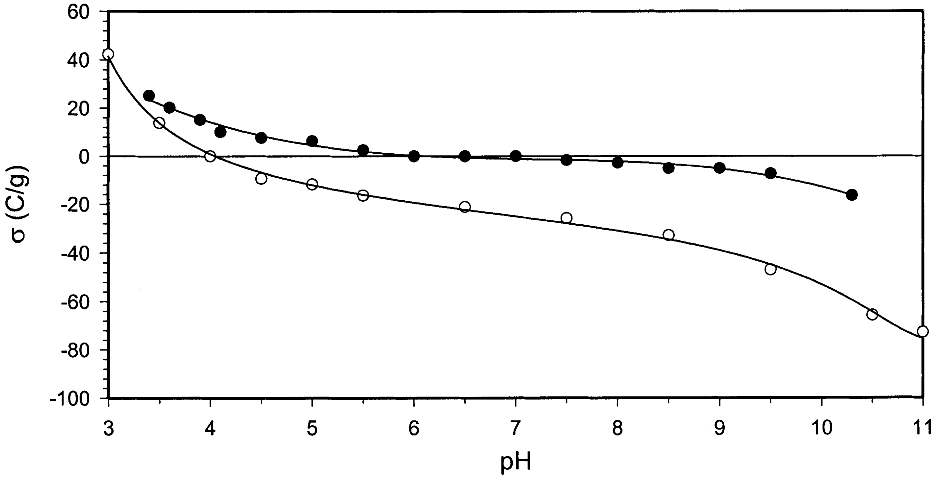


Fig. 2. Surface charge of sludge-based activated carbon (○) and the commercial activated carbon Chemviron GW (●) as a function of pH. Ionic strength: 10^{-3} M NaCl, 20 °C.

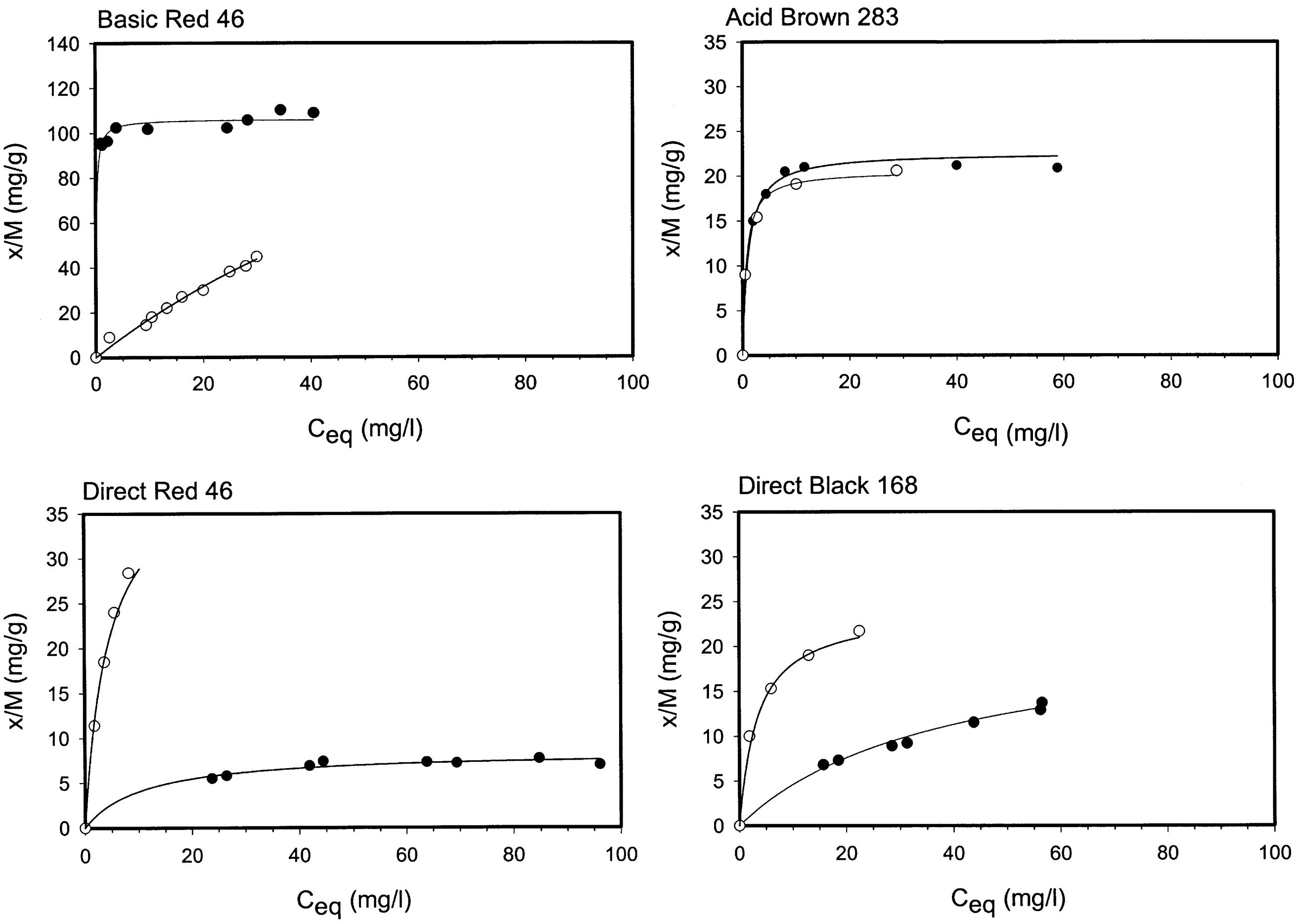


Fig. 3. Adsorption isotherms of Basic Red 46, Acid Brown 283, Direct Red 89 and Direct Black 168 on the sludge-based activated carbon (○) and the commercial activated carbon Chemviron GW (●).

where Q_m (mg/g) and b (l/mg) are isotherm constants obtained by polynomial regression fit for a particular solute–adsorbent combination and are shown in Table 5. The Langmuir isotherm equation was chosen because it has been commonly used to model data in wastewater adsorption treatment systems [28] and especially for dyes [29]. The Langmuir model (Table 5) gave satisfactory correlation coefficients ($r^2 > 0.979$) for the dye-activated carbon systems evaluated. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a dye molecule occupies a site, no further adsorption can take place at that site and a saturation value, i.e. Q_m, is reached which corresponds to the completion of a monolayer. At a low initial dye concentration $1 \gg bC_{eq}$ and hence $q = Q_m bC_{eq}$, which is analogous to Henry's law. The Langmuir model was therefore able to represent both the dye-AC systems showing limiting sorption capacities, and the linear behaviour observed in some of the dye-SB AC combinations evaluated (Fig. 3).

The different shapes of the adsorption isotherms are due to the different porous structures of adsorbents and of the adsorbate–adsorbent interactions. Isotherms having a step increase in adsorption capacity and a well-defined plateau on completion of a monolayer of molecules, such as Acid Brown 283 on SB AC or Chemviron GW, are associated with very high adsorption affinity and relatively strong adsorbent–adsorbate interactions [30].

Table 5
Langmuir parameters for the adsorption of dyes on the sludge-based and the commercial activated carbon Chemviron GW

Activated carbon	Dye	b (l/mg)	Q_m (mg/g)	r^2
Sludge-based	Basic Red 46	0.01	188	0.988
	Acid Brown 283	1.40	20.5	0.995
	Direct Red 89	0.17	49.2	0.999
	Direct Black 168	0.29	28.9	0.995
Chemviron GW	Basic Red 46	7.20	106	0.993
	Acid Brown 283	1.03	22.0	0.993
	Direct Red 89	0.09	8.40	0.979
	Direct Black 168	0.03	18.7	0.993

The results in Fig. 3 indicate that SB AC, having a preponderant mesoporous character and the largest mean pore diameter (Table 4), is equivalent or superior to the commercial product in the adsorption of the anionic-type dyes, i.e. the acid dye (Acid Brown 283) and the two direct dyes

(Direct Red 89 and Direct Black 168). Chemviron GW, with a S_{BET} four-fold higher than that of SB AC (Table 4), was only clearly superior in the adsorption of Basic Red 46, a dye molecule of the basic cationic type, and without anionic solubilising groups (Fig. 1).

The lack of correlation between the adsorptive capacity and the physical properties of an AC has been reported in the literature for a variety of solutes and activated carbon types. With regard to the adsorption of dyes, Walker and Weatherly [31] reported that only 14% of the S_{BET} of a commercial activated carbon (Chemviron F400, Calgon Carbon, UK) was available for the adsorption of three acid dyes with ionic weights of around 460 g/mol. The authors concluded that surface associated with the micropore structure was found to be redundant in the adsorption of large molecular weight compounds such as dyes. Regarding the relation between pore size and molecular sizes of adsorbates, Tamai et al. [32] reported that pore size rather than S_{BET} plays an important role in the adsorption of dyes with at least one dimension larger than the size of micropores. As shown in Table 2, Basic Red 46 is smaller than the size of micropores of AC. The high-adsorbed amounts of Basic Red 46 on Chemviron GW could hence be interpreted in terms of the relatively small steric size of dye molecules as compared with the size of micropores, and by the greater surface area of the commercial AC compared with SB AC (Table 4). Direct Black 168, with a molecular dimension greater than 2 nm (Table 2), the limiting diameter attributed to micropores, may be excluded from the microporous network and hence SB AC, which has a more opened porous structure, performed the best.

3.3. Effect of pH on the removal efficiency for dyes

Although pore size distribution and the relative size of the adsorbate molecules have a significant effect on adsorption capacity, the chemical nature of the adsorbent also plays a major role. To investigate the role of surface chemistry on the adsorption capacity of dyes, the effect of equilibrium pH was studied. The experiments were carried out by varying the initial pH, under a constant initial dye concentration of 100 mg/l and a carbon dosage of 4 g/l. The dependence of the equilibrium adsorption capacity of ACs for dyes on equilibrium pH is illustrated in Fig. 4.

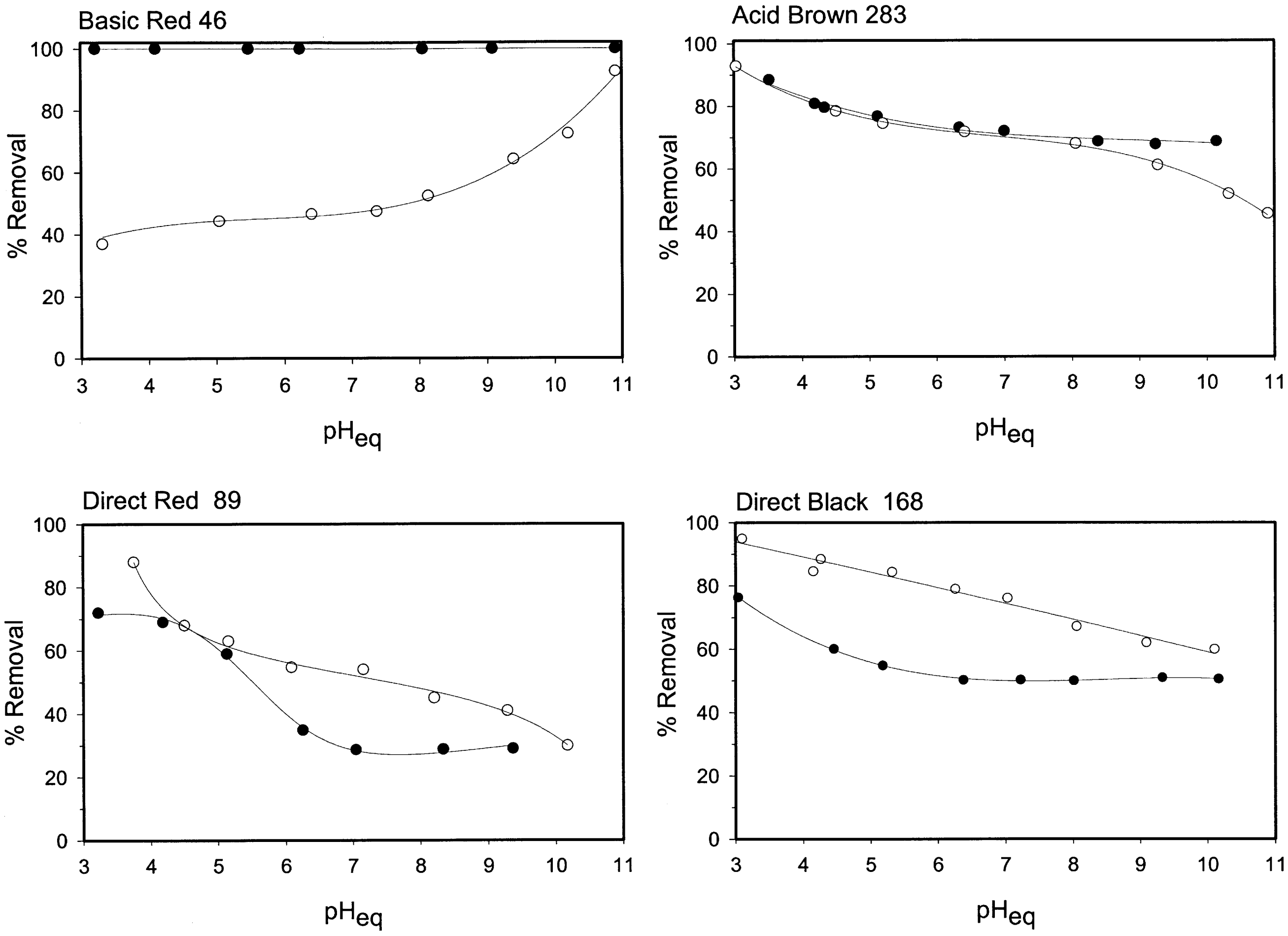


Fig. 4. Effect of pH on the adsorption capacity of dyes on sludge-based activated carbon (○) and commercial activated carbon GW (●). Experimental conditions: initial dye concentration 100 mg/l, activated carbon concentration 4 g/l.

The adsorbed amounts of the anionic dyes, i.e. the acid dye (Acid Brown 283) and the two direct dyes (Direct Red 89 and Direct Black 168), in SB AC gradually decreases with increasing pH, while the adsorption of Basic Red 46, a cationic dye, increases with increasing pH. The adsorption of the anionic-type dyes onto Chemviron GW is not influenced by pH values between 6 and 10 but it improves below pH 5. In addition, the commercial AC completely removed Basic Red 46 from solution and the amount of dye adsorbed remained constant at different pH values (Fig. 4).

The adsorption behaviour of the carbons towards dyes within the pH range investigated may be explained by the nature of the surface charge during the adsorption process and the surface charge density (σ) change with pH depicted in Fig. 2. For Chemviron GW, σ is only significantly modified at extreme pH values, i.e. for pH <4.5 and pH >10 (Fig. 2). This means that within the range of pH 5.5–9, the surface of Chemviron GW is almost neutral, which in turn makes the adsorption capacity remain almost constant within this pH range (Fig. 4), with no change in the electrostatic interaction between the solutes and the adsorbent surface. Adsorption capacity for the anionic dyes increases only at acidic pH levels (pH <5) because of electrostatic interaction with the positively charged surface.

The curve corresponding to SB AC (Fig. 2) shows that σ is strongly dependent on the solution's pH, changing from positive to negative for pH values above the $\mathrm{pH_{ZPC}} = 4$. Accordingly, the adsorptive capacity of SB AC for anionic dyes (Fig. 4) decreases as the activated carbon surface becomes negatively charged when the equilibrium pH is increased (Fig. 2). For Basic Red 46, the cationic dye investigated, the increase in the adsorptive capacity of SB AC with an increase in pH is attributable to a favourable electrostatic interaction between the dye molecule and the negatively charged surface. However, with respect to the electrostatic interaction between dye molecules and the surface of SB AC, the influence of electrostatic repulsion on the adsorption appears to be moderated, because the dyes still adsorb in spite of the opposite charge on the SB AC surface as a function of solution pH. Accordingly, and in agreement with the results reported by Dai [33], there may be a participation of non-specific dispersion interactions between AC and the ionic dyes.

4. Conclusions

It is possible to convert surplus biological sludge from wastewater treatment operations into activated carbon by thermal treatment in the presence of sulphuric acid, with a significant increase in surface area when compared to the raw sludge. The SB AC is mainly mesoporous in nature and acidic in character, while a conventional AC used as reference was found to be more microporous and hydrophobic. Due to the lower extent of development of microporosity, SB AC does not match the quality of commercial products in terms of surface area measured by nitrogen adsorption. However, half of the specific surface area of commercially available AC was found to be redundant in the aqueous adsorption of iodine.

The greater capacity of SB AC compared with the commercial AC to remove acid and direct dyes from solution is attributed to its wider pore size distribution. Similarly, the relative lower removal efficiency for Basic Red 46, is attributable to the relatively small steric size of the dye molecules as compared with the size of the micropores and by the greater surface area of the commercial adsorbent.

The presence of acidic surface functional groups in SB AC plays an important role in determining the extent of adsorption as a function of solution pH. The results obtained suggest that non-specific interactions play an important role in the adsorption of dyes in SB AC, since adsorption is still high in spite of the opposite surface charge as a function of the solution pH.

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