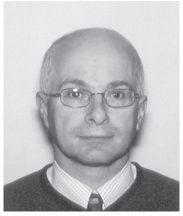
Journal of the University of Chemical Technology and Metallurgy, 40, 3, 2005, 175-192



DECOLOURISATION OF WATER/WASTEWATER USING ADSORPTION
(REVIEW)

S. J. Allen[1], B. Koumanova[2]

[1] *Queens University of Belfast, David Keir Building,*
Stranmillis Road, Belfast BT9 5AG, UK
[2] *University of Chemical Technology and Metallurgy,*
8 Kl. Ohridski, 1756 Sofia, Bulgaria
E-mail: bogdana@uctm.edu

Received 06 Juny 2005
Accepted 25 July 2005

ABSTRACT

Growing concern about environmental issues has prompted the textile industry to investigate appropriate and environmentally friendly treatment technologies. Waste aqueous effluent containing colour compounds causes serious environmental problems. A large variety of dyestuffs can be found in real effluents such as acid, basic, reactive, direct, etc. It has been estimated that about 9 % of the total amount (450 000 tons) of dyestuffs produced in the world are discharged in textile wastewater. The most frequently applied adsorbent for the removal of organic pollutants in wastewaters is currently activated carbon. However, activated carbon is an expensive material. The use of alternative and perhaps cheaper adsorbents is attractive. This review evaluates a number of different adsorbents and types of dyes. The review also outlines some of the fundamental principles of dye adsorption onto adsorbents. These subjects are central to the understanding of the adsorption processes occurring with different adsorbents.

Keywords: textile wastewater, adsorption, decolourisation, activated carbon, low-cost adsorbents.

INTRODUCTION

Dyes are chemicals which on binding with a material will give colour to the material. Dyes are ionic, aromatic organic compounds with structures including aryl rings which have delocalised electron systems. The colour of a dye is provided by the presence of a chromophore group. A chromophore is a radical configuration consisting of conjugated double bonds containing delocalised electrons. Other common chromophoric configurations include azo (-N=N-), carbonyl (=C=O); carbon (=C=C=); carbon-nitrogen (>C=NH or -CH=N-); nitroso (-NO or N-OH); nitro (-NO$_2$ or =NO-OH); and sulphur (C=S). The chromogen, which is the aromatic structure normally containing benzene, naphthalene or anthracene rings, is part of a chromogen-chromophore structure along with an auxochrome. The presence of ionising groups known as auxochromes results in a much stronger alteration of the maximum absorption of the compound and provides a bonding affinity. Some common auxochrome groups include - NH$_3$, - COOH, - HSO$_3$, - OH [1]. A detailed classification of dyes including some structures is provided in The Colour Index (C.I.) [2].

Coloured dye wastewater arises as a direct result of the production of the dye and also as a consequence of its use in the textile and other industries. There are more than 100,000 commercially available dyes with over 7 x 10^5 tonnes of dyes produced annually [3]. It is estimated that 2 % of dyes produced annually are discharged in effluent from manufacturing operations whilst 10 % was discharged from textile and associated industries [4]. Use of reactive dyes is increasing [5]. The rapid growth rate in the use of reactive dyes is due to the increasing use of cellulosic fibres and the technical and economic limitations of other dyes used for these fibres [5-6].

Neglecting the aesthetic problem, the greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water which interferes with the growth of bacteria to levels insufficient to biologically degrade impurities in the water [7]. Colour in effluents can cause problems in several ways: dyes can have acute and/or chronic effects on exposed organisms depending on the exposure time and dye concentration; dyes are inherently highly visible meaning that concentrations as low as 0.005 ppm capture the attention of both the public and the authorities [8]; dyes absorb and reflect sunlight entering water and so can interfere with the growth of bacteria and hinder photosynthesis in aquatic plants [9].

COLOUR ADSORPTION

Adsorption techniques for wastewater treatment have become more popular in recent years owing to their efficiency in the removal of pollutants too stable for biological methods. Adsorption can produce high quality water while also being a process that is economically feasible [10]. Decolourisation is a result of two mechanisms – adsorption and ion exchange [9], and is influenced by many factors including dye/sorbent interaction, sorbent surface area, particle size, temperature, pH and contact time.

Physical adsorption occurs when weak interparticle bonds exist between the adsorbate and adsorbent. Examples of such bonds are van der Waals, Hydrogen and dipole-dipole. In the majority of cases physical adsorption is easily reversible [11]. Chemical adsorption occurs when strong interparticle bonds are present between the adsorbate and adsorbent due to an exchange of electrons. Examples of such bonds are covalent and ionic bonds. Chemisorption is deemed to be irreversible in the majority of cases [11]. Suzuki [12] covers the role of adsorption in water environmental processes and also covers the development of newer adsorbents to modernise the treatment systems and the role modelling of the findings plays in their development. Most adsorbents are highly porous materials. As the pores are generally very small, the internal surface area is orders of magnitude greater than the external area. Separation occurs because differences in molecular mass, shape or polarity causing some molecules to be held more strongly on the surface than others or because the pores are too small to admit the large molecules [13].

Activated carbon. The main adsorbent used in industry is activated carbon. Different physical forms of activated carbon are produced depending on their application: granular (GAC) forms to be used in adsorption columns and powder (PAC) forms for use in batch adsorption followed by filtration [14].

The adsorption of two basic dyes, Maxilon Schwarz FBL-01 (MS-300) and Maxilon Goldgelb GL EC (MG-400), from aqueous solution by granular activated carbon and a natural zeolite in batch processes demonstrate that the activated carbon has a much stronger affinity for the dyes than the zeolite by a factor of two [15]. Meshko et al. [15] continue that the saturation capacities for both adsorbents for MG-400 are lower than for MS-300, because of the higher concentration of the active coloured material in the commercial salt of MG-400. The major component in MG-400 is a branched molecule which is also present in MS-300 but in significantly lower levels. It is therefore suggested that the molecules of MG-400 are probably unable to penetrate easily into the pores of the adsorbents whereas the molecules of MS-300 will have less hindrance. Overall, the size of both dye molecules is such that the adsorption is hindered and capacity is reduced due to pore blockage. The higher adsorption capacity of the activated carbon is attributed to the better pore size distribution in comparison to that of the zeolite.

Walker and Weatherley [16] measured the kinetics of acid dye adsorption onto a granular activated carbon. They report that a single value of a solid diffusivity could be used to describe the adsorption decay curves for constant mass contacting systems. However a decrease in solid diffusivity was required for systems with different initial dye concentrations. Chemisorption was suggested as the likely mechanism for the acid dye removal from water. In a separate paper [17], Walker and Weatherley report that the adsorption of the acid dyes by granular activated carbon in a fixed bed contacting system was characterised by shallow breakthrough curves suggesting a large mass transfer zone and the possible inefficient use of the carbon.

The adsorption of dyes onto carbon can depend upon surface charge on the carbon in the presence of water.

This will be close to neutral [18] and physical adsorption will predominate. Hence, active carbons will demonstrate a high capacity for both acid and basic dyes [18].

Choy et al. [10] considered the adsorption of acid dyes onto granular activated carbon and presented an analysis of the equilibrium adsorption in single component and multicomponent solutions. The data were analysed for three dyes using the Langmuir, Freundlich, Redlich-Peterson, Tempkin and Dubinin-Radushkevich isotherms. In their work the Redlich-Peterson isotherm was demonstrated to provide the best correlation for the sorption process. For the multicomponent isotherm models, an extended Langmuir model proved to be successful in predicting the binary equilibrium data.

Al-Degs et al. [19] investigated the effect of carbon surface chemistry on the adsorption of three reactive dyes in aqueous solution. In this work, the adsorption capacities for anionic reactive dyes, namely Remazol Golden Yellow RNL (Reactive Orange 107), Remazol Red RB (Reactive Red 198) and Remazol Black B (Reactive black 5) were determined using Filtrasorb 400 activated carbon. Under the same conditions, the adsorption capacity decreases in following manner: Remazol Yellow>Remazol Black>Remazol Red.

The adsorption capacity for reactive dyes increased with a decrease in the carbon particle diameter. At a particle size range of 300-500 mm the values of saturation capacities are reported as 1111, 434 and 400 mg g^{-1} for reactive yellow, reactive black and reactive red, respectively. F-400 has a high adsorption capacity for these dyes compared to chitosan where reported values are 380, 179 and 87 mg g^{-1} for reactive red, reactive yellow and reactive black at a particle size of 250-420 mm, respectively [20-21].

Al-Degs et al. [19] indicate that the adsorption capacity for Remazol dyes on granular activated carbon F-400 was reduced upon mixing in multi-component solutions. The results also show that carbon affinity was still higher for remazol yellow followed by remazol black and is lowest for remazol red. This effect was also reported in a study of three dyes (anionic character) in binary and ternary mixtures. The adsorption capacity of the individual dye from any mixture was lower than sorption from a single component system for all dyes studied [22]. Allen et al. [23] considered the competitive adsorption of three basic dyes. The results showed that the adsorption capacity of an individual dye decreased in the presence of a second or a third dye. The reduced capacities can be attributed to a number of factors including: interaction between the dyes in solution; change of the adsorbent surface charge due to adsorption; competitive adsorption between the dyes for active sites on the carbon surface where displacement effects replace the other dyes from the adsorption sites. At the beginning of the adsorption process, remazol yellow is the first to react with the surface of the activated carbon. This in turn may change the surface charge and surface chemistry of the carbon which will decrease the surface sites available to the remaining two dyes in the mixture. The large decrease in affinity of carbon for red, after mixing with black (system 3), is in contrast with the trend found for red in system 2 (Table 1). Here a relatively high adsorption value is found which can be explained by a low competitive behaviour between remazol yellow and remazol red when compared to system 3.

Undoubtedly, the pH value of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. Any oxide surface creates a charge (positive or negative) on its surface. This charge is proportional to the pH of the solution which surrounds the oxide particles. A convenient index of the propensity of a surface to become either positively or negatively charged as a function of pH is the value of the pH required to give zero net surface charge. This value is called point of zero charge (pH_{ZPC}) [24-25]. pH_{ZPC} is a critical value for determining quantitatively the net charge (positive or negative) carried on the activated carbon surface during adsorption of reactive dyes. Activated carbon has a high adsorption capacity or reactivity which arises from the complexity of the chemical surface groups compared to other surfaces. The surface of carbon materials can contain not one but, at least, five markedly different

Table 1. Adsorption capacities of activated carbon for Remazol Yellow, Remazol Black and Remazol Red.

	Dyes	Concentration range (mg dm^{-3})	Remazol Yellow	Remazol Black	Remazol Red
single			714	278	213
system 1	RY +RB	50-1000	600	160	----
system 2	RY+ RR	50-1000	590	----	185
system 3	RB + RR	50-1000	----	230	80
system 4	RB+ RY+ RR	50-1000	590	140	65

types of surface groups such as carboxylic, lactonic, phenolic, carbonyl and etheric types [26]. This diversity of surface groups makes the surface chemistry (acid-base character) much more versatile than that of other adsorbents [26].

Carbon surfaces acquire a "basic" character upon high-temperature (>973 K) heat treatment [27]. Most carbons contain a small amount of inorganic impurities that can influence their acid/base responses in solution [28]. Nevertheless, the pure organic portions alone have been shown to manifest their surface basicity in several ways [29] such as a pH value above 7, a positive external surface charge and acidic uptakes. The adsorbent (F-400) showed a pH value of 8.1 [29-30]. Most carbon materials have a higher surface basicity than surface acidity [31]. It should be noted that activated carbon materials have been categorised into H and L carbons according to their pH in a bulk solution. H carbon adsorbs more H^+ ions than OH^- and produces a suspension which has an alkaline property ($pH_{solution} > 7.0$) and a positive zeta potential. In contrast, an L carbon has been shown to produce a bulk acidic suspension and to exhibit a negative zeta potential [32].

The pH for the adsorption solutions (i.e. the pH of the dye solution and carbon particles after equilibrium) was increasing the positive charges on the surface of the F-400. This has the effect of attracting more negatively charged functional groups located on the reactive dye during the adsorption process. This is clearly indicated by the high adsorption capacity of F-400 for both H^+ and OH^- ions (amphoteric behaviour) and there is, as a result, an acid-base behaviour. This behaviour enables the activated carbon to manifest a reactivity for many organic and inorganic adsorbates. Depending on this property, it can be suggested that most of the adsorption behaviour for the reactive dyes was due to this acid-base reactivity. At any specific dye solution pH, F-400 will react either as an acid (positive surface) or base (negative surface). This means, that even though F-400 has an amphoteric property it doesn't show both reactivities at the same time.

The experimental results presented by Al-Degs et al. [19] indicate that the F-400 active carbon has a point of zero charge at pH 7.2. The measured equilibrium pH values of the three reactive dye solutions used in the adsorption studies were 5.5, 5.0 and 5.0 for reactive yellow, reactive black and reactive red, respectively. These pH values strongly indicate that F-400 has a net positive surface charge as equilibrium $pH < pH_{zpc}$. This positive surface has the effect of attracting the negative portion of the reactive dyes. A similar type of mechanism was postulated to explain the adsorption of methylene blue dye (cationic dye) on activated carbon at high pH. The reason was attributed to the presence of negatively charged carboxylate anionic surface functional groups on the carbon [32].

Activated carbon made from delayed petroleum coke is considered to be effective in the removal of colour from pulp bleaching water [33]. Methylene blue adsorption capacity of the activated petroleum coke was ten times greater than that for the raw petroleum coke. Activated carbons produced from agricultural such as silk cotton hull, coconut tree sawdust, sago waste, maize cob and banana pith various agricultural wastes have been used for the removal of dyes from aqueous solution [34]. However, despite the overriding influence of the nature of raw materials on the characteristics of the finished product, the search for low cost more environmentally friendly adsorbents has lead to the use of cocoa shell, coconut shell, fruit stones, newspapers, old tyres and basically any carbonaceous material remaining from industrial and/or municipal processes [35]. Choice of raw materials depends on what is available locally at low cost, provided it will lead to the production of a carbon with reasonably large adsorptive capacity that is economically viable.

Equilibrium and kinetic studies of reactive dye and basic dye adsorption by lignite based activated carbons [36] and commercial activated carbon [37,38] have been undertaken. In these investigations two resistance diffusion models have successfully modelled the adsorption processes. Allen and Duggan [39] report on the production of a range of chemically modified lignite chars. This work and work by Duggan [36] suggest that the sorption capacity of lignites for basic dyes can be enhanced by chemical activation with a number of transition metal salts. For example, a lignite char chemically activated by sodium tungstate had an increased capacity for basic red 22 compared with untreated lignite. The untreated lignite had a greater capacity than charred lignite with no chemical activation. Chars which had the greatest BET surface area did not always have the highest adsorption capacities.

Chitin and chitosan. Chitin is the second most abundant natural carbohydrate polymer next to cellulose

[40]. Chitin is a naturally occurring derivative of cellulose, where the C_2 hydroxyl group has been replaced by the acetyl amino group -$NHCOCH_3$. The major derivative of chitin is chitosan which refers to a family of polymers derived from chitin by deacetylation. Chitin and chitosan are adsorbents which can contain amine or amide nitrogen in varying proportions. These groups can lead to the adsorbents having a larger adsorption capacity for acid dyes or anionic dyes. Adsorption can occur by van der Waals attraction, hydrogen bonding and coulombic attraction [41,42]. Chitin will display no significant attraction to basic dyes [43 -46].

Table 2. Maximum monolayer adsorption capacities of some dyes on various adsorbents.

Adsorbent	Dyes	Approximate uptake (g kg^{-1})	Ref
Activated carbon	BB3, BR22	448, 500	157
Activated carbon	Maxilon Schwarz FBL-01 Maxilon Goldgelb GL EC	309 159	15
Activated carbon	AR114, AY76, AB80	101, 101,129	10
Activated carbon (F400)	AB277, AR361, AO156	537, 535, 852	38
Activated carbon	Deorlene yellow, AB25	200, 160	158
Activated carbon	RR 222	50	20
Activated carbon (F400)	RO107, RBk5, RR198, BB9	1111, 434, 400, 533	37
Activated carbon (C207)	RO107, RBk5, RR198, BB9	426, 109, 123, 474	37
Activated carbon (EA207)	RO107, RBk 5, RR 198, BB9	384, 96, 72, 436	37
Activated carbon (Centaur)	RO 107, BB9	200, 314	37
Activated carbon (F400)	RR158	275	104
Activated carbon	AO10	2-6	159
Activated sludge	RY 2	333	48
Activated sludge	RB 2	250	48
Activated carbon (coir pith)	Congo Red	7	160
Bacteria	RY 2	52-124	159
Bagasse pith	BB3, BR22, AB25	62, 67, 22	157
Banana pith	Acid Brilliant Blue	4-5	114
Banana and orange peel	MO, MB, RB	14-21	116
Banana and orange peel	CR, MV, AB	6-18	116
Bone char	AB277, AR361, AO156	476, 508, 477	38
Carbon, peat, alumina	AB 25	83-99	157
Carbonaceous waste	Ethyl orange, AY36, AB113	198, 211, 219	134
Char, Lignite, Coal, Carbon	DBr1	6, 4, 2, 8	102
Chitin	MY 5, AB25,	52, 183,	161
Chitin	AB158, DR84	216, 44	161
Chitin	RR222	100	20
Chitosan bead (crosslinked)	RR189	1642-1936	162
Chitosan bead (crosslinked)	RB2, RR2, DR81	2498, 2422, 2383	47
Chitosan bead (crosslinked)	RO14, RY86	2171, 1911	47
Chitosan bead (crosslinked)	AO12, AR14, AO7	1955, 1940, 1940	47
Chitosan fibre (crosslinked)	AO2	1226-1678	163
Chitosan (non-cross-inked)	RB222, RY145, RR222	87, 179, 380	20
Chitosan (non-crosslinked)	RR222	1026-1106	164
Chitosan bead (non-crosslinked)	RR189	1189	162
Chitosan flake	AG25, AO10, AO12, AR18, AR73	645, 923, 973, 693, 728	52
Chitosan flake	RR158	310	133

Chiou et al. [47] report on the adsorption of four reactive dyes, three acid dyes and one direct dye onto cross-linked chitosan beads. The adsorption capacity values ranged from 1911 – 2488 mg g^{-1} at pH 3-4 and are presented in Table 2. The values are between 3 and 15 times and 3 and 27 times the adsorption capacities of a commercial activated carbon and chitin, respectively. In their paper the authors confirm that the adsorption conforms to a Langmuir isotherm and a pseudo-second order kinetic model. In addition, adsorption capacity appeared to increase with a decreasing pH of the solution. It is suggested that the chemisorption process controls the adsorption process. The -NH_2 group is easily protonated in acid solution to become –NH_3^+. This has a strong electrostatic attraction with the coloured dye anions. Similar results are reported for the adsorption of RB2, RY2 and Remazol Black B on a biomass [48, 49]. The -NH_2 groups and hydroxyl groups can serve as coordination and electrostatic interaction sites [50].

Chitin contains the amide group –CO-NH- which cannot be easily protonated. The electron withdrawal by the carbonyl group makes the nitrogen of the amide group a poorer source of electrons than that of the amine group. Fewer electrons are available for sharing with a hydrogen ion and therefore the amide is a much weaker base than the amine group. Hence in chitin there is less electrostatic attraction between the chitin and the dye anion. The adsorption capacity of basic violet 3 is essentially zero at pH 3.0 [47].

The concentration decay profiles for the batch adsorption of three reactive dyes onto chitosan are correlated by three simple kinetic models: pseudo first order; pseudo second order; the intraparticle diffusion model [51]. The intraparticle diffusion model best describes the results. The rate parameter for the adsorption of the reactive dye decreases with increasing particle size of chitosan.

Wong et al. [52] compared the uptake of acid dyes onto chitosan derived from deacetylated crab shell chitin. Their results were analysed by Langmuir, Freundlich and Redlich-Peterson isotherm equations using linearised correlation coefficient. They suggest that the Langmuir isotherm gave the best correlation for the adsorption for four of the dyes whilst a composite

Freundlich isotherm gave an excellent correlation for one. Using five different non-linear error analysis methods, the order of isotherm selection was changed showing that the Redlich-Peterson equation had the lowest error values for all five dyes. Monolayer capacities ranged from approximately 645 to 925 mg g^{-1}. The difference in capacities was attributed to the difference in the molecular size of the dye molecules and the presence of different numbers of sulphonate groups present on each dye. The monovalent and smaller dyes are reported to have superior adsorption capacities due to the increase in the dye/chitosan ratio in the system which enabled deeper penetration of the dye molecules into the internal pore structure of the chitosan.

Diatomite. Diatomite is siliceous sedimentary rock consisting principally of the fossilized skeletal remains of the diatom [53]. Total surface area of diatomite is around 28 m^2 g^{-1}. More importantly however is the presence on the silica surface of silanol groups that spread over the matrix of the silica [54]. The silanol group is a very active group, which can react with many polar organic compounds and various functional groups. This property makes it a possible adsorbent for many dyes.

The feasibility of using diatomite for the removal of Cibacron reactive black C-NN (RB) and reactive golden yellow MI-2RN dye as well as methylene blue, a basic dye is reported [55]. Unfortunately, the molecular structure of Cibacron reactive black and yellow dye is not released, however, it is expected that most Cibacron reactive dyes contain a reactive halotriazinyl amine group that has two or more labile chlorine atoms activated by the electron withdrawing action of the three N atoms [55]. Diatomite has surface charges which may arise from chemical reactions at the surface due to the presence of ionisable functional group such as –OH, -COOH, -SH and $-NH_2$. The ionisation of such groups results in electric charges [26, 56]. The surface charge caused by these surface chemical reactions is known as the surface charge density which is dependent on the degree of ionisation and on the pH of the system. For diatomite the zero point of charge (pH_{ZPC}), the pH at which the total charge from the cations and anions at the adsorbent surface is equal to zero, occurred at pH value of 6.2. The surface charge density decreased as the pH increased. Hydroxyl groups present on the surface of the diatomite can gain or lose a proton, resulting in a surface charge that varies with changing pH. At low pH, surface sites are protonated and the surfaces become positively charged. At high pH, the surface hydroxides lose their protons and the surface becomes anionic. Maximum percentage removal of methylene blue took place at pH 10-12, and the removal rate decreased with the decrease in pH.

Lower adsorption of methylene blue at low pH is probably due to the presence of excess H^+ ions competing with the cationic groups on the dye for the adsorption sites. The percentage removal of the hydrolysed reactive dyes decreased with increase in pH (above pH 9), and the maximum removal rate was achieved under acidic conditions (pH 3). Consequently, the percentage colour removal of the hydrolysed reactive black dropped from 40 to 13 % and a change from 28 to 0.1 % was estimated for reactive yellow. As the surface charge density decreases with an increase in the solution- pH ($pH > pH_{ZPC}$), the electrostatic repulsion between the positively charged dye (methylene blue) and the surface of the diatomite is lowered, which may result in an increase in the rate of adsorption [55, 57]. At lower pH, $pH< pH_{ZPC}$, the percentage colour removal of hydrolysed reactive dyes was relatively high, which may be attributed to the presence the positive charge of the diatomite. It is proposed that the adsorption of methylene blue, hydrolysed reactive black and yellow occurs by the conversion of the surface of diatomite from a positive to a negative charge for the case of cationic dyes, and from negative to positive for the anionic dyes in the event that the pH values of the solution become higher or lower than pH_{ZPC}, respectively. It can therefore be said that coulomb interaction plays an important role in the adsorption of such dyes onto diatomite [26]. The percentage colour removal of the dyes in this investigation remained constant in the pH range from 4 to 9 (outside the pH_{ZPC} value).

The effect of initial dye concentration on the ability of diatomite to adsorb dyes from solution suggests that the percentage colour removal of methylene blue decreased when the initial dye concentration increased. However, it remained constant in the dye concentration range 100 to 1000 mg dm^{-3} for the reactive dyes. The adsorption isotherm data were further analysed using the Langmuir and Freundlich isotherm, which are the most frequently applied sorption isotherm models [55, 58]. The adsorption behaviour of methylene blue, hydrolysed reactive black and yellow dyes were favourable. It seems that diatomite has a high selectivity for basic and reactive dyes. The Langmuir isotherm was unable to explain the adsorption process for the reactive dyes but was suitable for the basic dye. It is important to recognise that the mechanism of dye adsorption on diatomite cannot be concluded directly from the Langmuir or Freundlich fitting, however, it can be concluded that the adsorption isotherm of methylene blue exhibits Langmuir behaviour, which indicates a monolayer adsorption and the adsorption of the hydrolysed reactive black and yellow dyes was best represented by the Freundlich model, which indicates a heterogeneous surface binding [55, 58].

FTIR spectra shifts or changes in peaks indicate interactions of the dyes with silanol groups, and can be interpreted as adsorption on neutral sites [59]. According to the FTIR spectra and the pH dependency of the adsorption of methylene blue (MB), hydrolysed reactive black (RB) and reactive yellow (RY) dyes, there is an electrostatic (columbic) attraction between MB^+ and the negative charge on the surface of diatomite at high pH (i.e. pH 11). Moreover, an electrostatic attraction between RB^-, RY^- and the positive charge on the surface of diatomite at low pH is evident. Adsorption of methylene blue onto diatomite can be attributed to the formation of surface hydrogen bonds between the surface hydrogen bonds of the hydroxyl group on the diatomite surface and the nitrogen atoms of methylene blue.

The affinity of methylene blue, hydrolysed reactive black and yellow dyes for diatomite were methylene blue > hydrolysed reactive black > hydrolysed reactive yellow. However, at fixed pH (pH = 3), the surface charge density of diatomite is constant and independent to types of dye. So the columbic attraction of the positively charge on the surface of diatomite is the same for both reactive dyes. Therefore, the chemical structure (shape, number of active groups, stability of a negative char) of the dye must give the difference in the affinity of these reactive dyes toward diatomite [55].

In a comparison to activated carbon adsorbent, FS-400 seems to have a better affinity toward the reactive dyes than diatomite. In contrast, diatomite has a better affinity than activated carbon (FS-400) toward basic dyes; however the adsorption capacity of FS-400 is greater than diatomite for methylene blue adsorption [55].

Silica. Silica is used as an adsorbent mainly in granular form. Sorbsil silica gel is reported to adsorb basic dyes [60-61]. The rate of adsorption of Astrazone Blue, a basic dye, on Sorbsil Silica has been studied in batch adsorbers. Parameters studied include particle size, initial dye concentration, agitation and dye solution temperature. The rate-controlling step is mainly intraparticle diffusion, although a small boundary layer resistance is experienced. The process shows the same general form of an initial steep rise in adsorption with time and then a rapid levelling off as equilibrium is established. In all cases 90% of the equilibrium value is reached after 240 minutes of contact [62].

Depending on the theoretical meaning of the $pH_{Z.P.C}$, one expects a low adsorption capacity with silica or clay (high silica content) adsorbents toward anionic reactive dyes. Silica adsorbents have a low $pH_{Z.P.C} \approx 2$ [63], therefore, at moderate pH values of 5-8, the surface will carry a net negative charge as a result of which the anionic dye particles will be repulsed from the surface. This may explain the low adsorption capacity (36 mg g^{-1}) for a reactive red dye that was reported [20].

Silica modified with humic acids has been used to adsorb indigo carmine dye [64]. In this work two distinct humic acids, one extracted from a Brazilian peat and a second commercial humic acid, were attached onto a silica gel modified with aminopropyltri-methoxysilane. The ability of these two materials to adsorb the dye was followed through a series of isotherms described by a modified Langmuir equation. The maximum uptake for the two materials was 6.82×10^{-4} and 2.15×10^{-4} mol g^{-1} respectively. The change in capacity is attributed to the presence of different concentrations of chelating groups such as $-NH_2$, -OH, -COOH, $-CONH_2$ and –SH on the modified surface of the silica.

Perlite. Perlite is an amorphous siliceous mineral silicate and the feasibility of the electroadsorption of acilan blau dye by perlite-activated carbon mixtures suggests that the process is better than activated carbon adsorption alone [65]. A carbon: perlite ratio of 8:1 is the optimum. Total dye removal is possible with a smaller amount of carbon in a lower bed height. Removal efficiency is improved increases with increasing applied potential. Langmuir isotherm model correlated the results well for both adsorption and electroadsorption processes.

Dolomite. Thomas [66] discussed the use of carbonate rocks, (dolomite, and calcite), for adsorption. Dolomite is a common double carbonate mineral of an ideal formula $CaMg(CO_3)_2$, rather than a mixture of calcite and magnesite. The dolomite structure can be visualised as alternative layers of calcite and magnesite [67].

Staszczuk et al. [68] developed the idea of thermal decomposition of dolomite and that the char temperature should be approximately 780-840°C, for the decomposition of magnesium carbonate to occur. Partial decomposition of dolomite at 800°C leads to changes in the chemical composition of the surface and in the porosity of the material.

Walker et al. [69] report on the kinetics of adsorption of a reactive red dye by dolomite and dolomitic adsorbents. Results indicate that dolomite and charred dolomites have the potential to act as adsorbents for the reactive dye. The removal rate appears to be dependent on both an external mass transfer process and some intraparticle diffusion. A comparison is made with uptake using a Chemviron activated carbon indicating that the adsorption by the dolomite char is greater than that of activated carbon and untreated dolomite.

Fuller’s earth. Fuller’s earth is a natural clay which can contain variable amounts of dioctahedral smectites, natural zeolites and other sepiolites. The main content is magnesium and aluminium silicates. The clay is given an open porous structure by heating and drying processes. Methylene blue, a cationic dye, is shown to adsorb strongly onto four different Fullers earth samples of varying compositions [70]. Methylene blue adsorption appears to increases as the percentage of Al_2O_3 and CaO, Fe_2O_3 in the Fullers earth decreases and as the percentage of MgO and Na_2O increases. In this work the adsorption isotherm is divided into three regions: in the first region there is an S-shaped isotherm which corresponds to a slow increase, followed by a fast growth, and a region growing to a plateau at low dye loadings; in the second region, the dye in solution reaches zero with flocculation occurring; in the third stage an H type isotherm is observed [70]. Both the Langmuir and Freundlich equations gave good agreement. In a comparison the adsorption capacities of the Fullers earth samples were higher than those of a commercial activated carbon. In addition the time to reach equilibrium is shorter.

Bentonite. Bentonite is a fine powder clay which normally requires activation by acid washing before it exhibits adsorptive properties. It can have montmorillonitic properties with a SiO_2:Al_2O_3 ratio of 3.77 [71]. The clay has adsorbent properties and an alkaline pH due to the presence of sodium, potassium and calcium components. Bentonite has been used for dye removal form water [72]. In this work, peat, steel plant slag, bentonite clay, fly ash and activated carbon adsorbents were compared in batch kinetic studies, isotherm studies and column studies and the data evaluated for compliance with the Langmuir, Freundlich and BET isotherm models. Acid, basic and disperse dyes were used and the results showed high removals of acid dyes by fly ash and slag while peat and bentonite exhibited high basic dye removals. For the acid and basic dyes, the removals were comparable with that of granular activated carbon, while for the disperse dyes, the performance was much better than that of granular activated carbon [72].

The adsorption of methylene blue using activated and non-activated bentonites suggests an improvement in the adsorption capacity of the bentonite by activation with either treatment using sodium dodecyl sulphate (SDS) as an ionic surfactant or by thermal activation at 850°C. Batch adsorption tests demonstrated found that the effectiveness of bentonites towards methylene blue was thermal-bentonite > SDS-bentonite > natural bentonite. An increase in the microscopic bentonite platelets on treatment with SDS was the reason behind the higher uptake of the dye. Greater removal of dye occurred with an increase in bentonite concentration or initial pH value. The Freundlich isotherm model represented the experimental data well [73].

When a basic dye is adsorbed onto bentonite it forms a dye-clay complex or organoclay. Borisover et al. [74] report that these complexes are very suitable for the further adsorption of non-ionic or organic compounds such as atrazine and phenols. Organoclays are also useful in membrane processes where membrane fouling may be a problem [75-77]. Bentonite can be combined with ultrafiltration as a method for colour removal, methylene blue dye, from wastewater [78]. The hybrid process makes use of the adsorption abilities of the bentonite along with the abilities of the ulltrafiltration to remove colloidal particles.

The adsorption ability of bentonite can be improved when it is mixed with aluminium hydroxide polymers [71, 79]. The mixture of bentonite and aluminium hydroxide polymers enables the removal of more than 95 % of a soluble dye and 96 % of chemical oxygen demand whilst producing a sludge which can be easily removed by settling processes. After exchanging the sodium of the bentonite with polyaluminium hydroxide polycations and separation, a thermal treatment eliminates the polyaluminium hydroxide between the bentonite layers. This product can be used as the adsorbent for the adsorption of Supranol yellow 4GL, Erionyl red RS, Erionyl marine blue MR and Nylomine black C2RN in multicomponent mixtures [80]. Equilibrium was reached after twenty minutes. Different rate coefficients were obtained for the different dyes; this was attributed to the different affinities towards the reaction sites of the bentonite-polymer adsorbent. The supranol yellow proved to be difficult to remove. The sodium ion had no effect on the overall reaction reinforcing the assumption that the adsorption was onto the bentonite-polyaluminium hydroxide compound and not onto the bentonite layer itself [79].

Combinations of different clays, namely beige and brown sepiolites, calcium and sodium bentonites, with aluminium have been used to remove colour from pulp and paper wastewater [81]. It is reported that the clays tested were not efficient in removing colour when they were applied on their own. However, when alum was added an increase in removal was observed as compared to alum on its own or a clay on its own. A problem could be that the voluminous sludge which is created has poor settling characteristics. Acid activation did not improve the clay adsorption capacity.

The batch adsorption of a reactive dye, cibacron yellow LS-R, onto hydrotalcite is reported by Lazaridis et al. [82]. Hydrotalcite is a synthetic Mg-Al material which has good anionic exchange properties. Lazaridis et al. claim that no single kinetic model can fully describe the adsorption process at all times. At least three independent rate –controlling mechanisms appear to compete and will dominate at different stages of the sorption process. These are an external surface enhancement or film diffusion (early stages), a reaction stage which governs the subsequent and largest part of the process and finally a diffusion process which will considerably slow down the sorption rate. The rate of adsorption is sensitive to pH and ionic strength of the dye solution but almost insensitive to initial dye concentration.

Zeolite. Mezoporous materials such as sepiolite and zeolite which are highly porous materials have been used to adsorb three reactive dyes [83]. Adsorption isotherms for natural sepiolite exhibit a linear increase followed by a plateau region. Maximum adsorption occurs around 0-5 –1.0 g kg^{-1}. The results reveal that natural sepiolite appears to have little affinity for reactive dyes [83]. The natural zeolite appears to have a negative adsorption except for the red dye above 25 g m^{-3}. The azo dyes are excluded from the zeolite structure due to their larger size, whereas the other ions in solution and the water itself will adsorb into the structure increasing the apparent concentration of the dyes in the bulk solution which in turn leads to a negative adsorption [83]. Ozdemir et al. [83] went on to suggest that modification of the sepiolite and zeolite surfaces by quaternary amine surfactants will enhance the adsorption capacity. The surfactant hydrophobises the surface of the samples and also neutralises the negative charges on the surface.

Peat. Peat is a low-grade carbonaceous fuel containing lignin, cellulose and humic acids as its major constituents. These constituents are potentially very useful from an adsorption standpoint as they bear polar functional groups such as alcohols, aldehydes, carboxylic acids, ketones, and phenolic hydroxides which can all be involved in chemical bonding with the adsorbed pollutants. Peat has a polar character which lends itself to the adsorption of specific materials such as metals and polar organic molecules.

Peat is known to have excellent ion exchange properties similar to natural zeolites [84]. Leslie [85] studied the treatment of dyehouse effluent using a Hussong/Couplan wastewater treatment process based on peat moss. Murray [86], Khader [87] and Allen [88] present discussion on the equilibrium and kinetics of adsorption of colour removal from wastewater by peat.

It is suggested [89-91] that irreversible coulombic attraction and ion exchange is the mechanism for basic dye adsorption by adsorbents containing a high level of cellulose [42]. Conversely, it is possible that a coulombic repulsion of an acid dye (negatively charged) can occur due to the creation of a negative charge on the adsorbent surface in the presence of water [92]. Clearly therefore, the pH of the dye solution will alter the adsorption characteristics. Low pH values could enhance the adsorption capacity of a cellulose-based adsorbent towards an acid dye.

Adsorption of a cationic dye appears to increase with increase in pH consistent with a mechanism of adsorption by cation exchange with acidic functional groups. There are then more adsorption sites for cation uptake from solution. Similarly a decrease in pH produces more competition for adsorption between cations and the increased H^+ presence. As a result of this, cations will be desorbed.

There is a good correlation between the content of unesterified polyuronic acids in the cell wall of sphagnum peat and the cation exchange capacity. The adsorption of cations occurs by the formation of complexes with the carbonyl and nitrile groups in peat. The presence of humic acids in peat is primarily responsible for its ability to adsorb metals and other cationic species. Authors discussing the subject agree that the natural capacity of peat to retain cations is related to the pH of the solution [93]. Adsorption increases as the surface area of the organic substance increases which could explain the increase in adsorption capacity after humic acids were extracted from the peat and lignite [93].

Peat is shown to be a particularly effective adsorbent for basic dyes but has a lower capacity for acid dyes [25, 86-88, 94-99]. Single resistance models, which assume negligible intraparticle diffusion, were used to evaluate the contribution of external mass transfer resistance during the adsorption of dyes onto peat. For the range of process variables investigated, results indicated that the mass transfer coefficient was dependent on initial dye concentration and agitation speed. It was concluded that the assumption of a single external resistance to mass transfer only applies in the initial stages of the sorption reaction. After approximately twenty minutes contact time, deviation between experimental and predicted results showed the cumulative effect of intraparticle diffusion. The ability of the two-resistance film-pore diffusion model to describe the adsorption profiles of the dyes adsorbing onto peat was poor. The homogeneous solid diffusion model proved to be the most successful of the models used to describe the adsorption of basic dyes onto peat and lignite. The model highlighted the concentration dependence of solid diffusivity and the significance of external mass transfer resistance in the adsorption systems.

Sun and Yang [100] chemically modified a peat by mixing it with sulphuric acid, polyvinyl alcohol and formaldehyde to produce a peat-resin particle. The adsorption of basic magenta and basic brilliant green onto the modified peat resin particles exhibited deviation form the Langmuir and Freundlich isotherm. The pseudo-first order, pseudo-second order and intraparticle diffusion models were used to correlate the experimental data and the intraparticle diffusion model yielded the best fit. Initial dye concentration, particle mass and particle size all affected the adsorption rate processes. Diffusion rate increased with initial dye concentration and decreased with increase in particle mass. Diffusion rate increased with a decrease in particle size [100].

Lignite. Lignite is a member of the solid fuel family and is often referred to as brown coal. The surface area, porosity, functional groups, calcium and magnesium ion content all contribute to its adsorption properties. Lignite has a strong affinity for basic dyes [96, 98]. The lignite-cationic dye sorption process is facilitated by the presence of the humic acid groups in the lignite. The adsorption process is a function of the dye structure and the lignite structure. Different ions will experience different physical and electrical attractive and repulsive forces according to their structure, molecular size and functional groups. The process is a combination of ionic attraction/ repulsion, hydrogen bonding, ion-dipole forces, covalent bonds and van der Waals forces. The differential sorption capacity of coal based sorbents like lignite will in part be due to the grade of the coal. In other words, there is a relationship between the extent of the coalification and the inherent ion exchange capacity which may reduce as the coal ages [101]. During the coalification process there is a marked increase in the hydroxyl and carboxyl group content of the coal which may facilitate the increase in the ion exchange and sorption characteristics of the adsorbent.

The removal of a direct brown azo dye by lignite, charfines and bituminous coal suggested that the sorption interaction obeyed a first-order irreversible rate equation whereas the same dye would obey a first-order reversible rate equation for adsorption by Filtrasorb-400 [102]. The dye adsorption interaction was complex and intraparticle diffusion was not the only rate-limiting step. The isotherm data was fitted by a rearranged Langmuir isotherm. The ranking of the adsorbents in terms of colour removal capacity was activated carbon (7.69 mg g^{-1}> charfines (6.4 mg g^{-1}) > lignite (4.1 mg g^{-1}) > bituminous coal (2.04 mg g^{-1}). These values are much lower than the capacities for basic and reactive dyes.

In terms of the initial rate of adsorption, the uptake of the basic dyes onto peat particles was found to occur more rapidly than onto lignite. The magnitude of the external resistance to mass transfer was found to be dependent on initial solute concentration and agitation speed of the system. Increases in the solute concentration produced a decrease in values of external mass transfer coefficient, whereas, increasing the agitation speed resulted in their elevation.

In relation to intraparticle diffusion, values of the effective diffusivities calculated using both film-pore and film-solid diffusion models were found to be dependent upon the initial dye concentration. Results indicated that the effect of increasing the concentration of dye molecules in the liquid bulk was to decrease the values of diffusivity obtained. These trends in results were also observed in the values of external mass transfer coefficient determined and were thought to be due to the formation of micelles in dye solutions of high concentration. The resulting increase in size of adsorptive species would be responsible for the decrease in the initial rate of adsorption, and reduced surface mobility.

The relative effect of each resistance to mass transfer within an adsorption system is largely dependent on the method of contact employed. For batch adsorption systems, studies have shown that intraparticle diffusion controls the main course of the separation process and the results obtained for the adsorption of basic dyes onto peat and lignite is no exception. In fixed bed adsorption systems, where the boundary layer around the sorbent particles is fairly stagnant and thick, the external resistance to mass transfer is thought to have considerable effect. From results of sensitivity analyses it was concluded that the adsorption of Basic Red 22 onto lignite in columns is controlled by intraparticle diffusion. Since the mode of separation occurring within this system is predominantly chemisorption it may be postulated that surface diffusion effects augment the value of the effective diffusion coefficient obtained.

Kudzu. Kudzu (*Pueraria lobata*) is a rapidly growing, high climbing perennial leguminous vine. In 1970 this once helpful plant was classified as a weed in the United States and most information on it has come from attempts to eradicate it [103]. A study of the adsorption of basic dyes by Kudzu has been reported by Matthews [104]. Allen et al. [105] compared the optimised adsorption isotherm models for basic blue 3, basic yellow 21 and basic red 22 adsorption. Kudzu demonstrated a good capacity for basic dyes, although the capacity was not as high as for a commercial carbon. Adsorption capacity for basic dyes on kudzu was reduced upon mixing in multi-component solutions. The adsorption capacity of the individual dye from any mixture was lower than sorption from a single component system.

Koumanova et al. [106, 171] demonstrated the use of kudzu as a low-cost adsorbent for the adsorption of acid dye Erionil Marine Blau. The data show that the model of Freundlich is more suitable for the description of the adsorption equilibrium than that of Langmuir. A comparison of the rate constants and calculated by the pseudo-first and pseudo-second order kinetic models using the equations of Lagergren proves the applicability of the pseudo-second order equation. Intraparticle diffusion in the pore structure is proposed as a mass transfer mechanism. A diffusion rate parameter is proposed and is correlated with possible system variables including the influence of initial dye concentration, mass of the sorbent and rate of agitation [106].

The intraparticle diffusion model also described the experimental results. The transport of the adsorbate molecules to the micropores occurs through the diffusion in macropores and transitional pores. The diffusion process is described in the macropores, transitional pores and micropores. The values of the diffusion parameter in macropores are higher than those for the transitional and the micropore regions. The decrease in the pore sizes leads to the decrease in the free path of the molecules in the sorbent pores and hence to a decrease in the values of the measured intraparticle rate parameter. As pore dimensions decrease, the free path becomes smaller, with possible pore blockage occurring and hence the reduction in diffusion parameters [106].

Other adsorbents. In recent years there has been a considerable amount of research in finding cheaper alternatives to activated carbon. The removal of coloured organic material by adsorption onto low cost materials is reported by Bousher et al. [42]. Materials such as charred sawdust [107], carbonised wool waste [107], charred plant material [108], quaternized rice husk [109] and cassava peel char [110] have been found to be effective in the removal of a variety of dyes from water. Rajeshwarisivaraj et al. [111] produced carbon from Cassava, a short-lived perennial shrub. The carbon produced by H_3PO_4 activation was found to have a higher adsorption capacity for dyes than the carbon produced by physical activation. Materials that have been used in their natural state to adsorb heavy metals and dyes from solution include linseed cake [112], sunflower stalks [113], banana peel [114-115], orange peel [116-117], Fuller's Earth [118], chitin [119], eucalyptus bark [120], wood [121-123], maize cob [124, 125], biogas waste slurry [126], water hyacinth roots [127], waste red mud [128], fly ash and coal [129, 130]. Thermotreated mineral sorbent has been used for the adsorption of acid and direct dyes [169]. Ion exchange fibres also have been studied [170]. Reviews of equilibrium and kinetic studies of dye adsorption by eggshell membrane [131], *Rhyzopus oryzae* [132], are reported. Neem leaf powder is reported to be an effective adsorbent of a brilliant green dye [133].

Jain et al. [134] described the use of industrial waste products as adsorbents of anionic dyes. In this work, a number of low cost adsorbents were prepared from the steel and fertilizer industries. These adsorbents were then used to adsorb three anionic dyes from water. Their results suggest that inorganic waste such as blast furnace dust, sludge and slag from steel plants are not suitable for the removal of organic materials, whereas a carbonaceous adsorbent prepared from the fertilizer industry had a good uptake of the anionic dyes which approximated to about 80 % of a commercial activated carbon.

Janos et al. tested brown coal fly ashes as adsorbents of both basic (cationic) and acid (anionic) dyes [135]. Both classes of dye are adsorbed to a similar extent by the fly ash. The dye sorption was decreased by the presence of organic solvents. Low concentrations of surfactants enhanced the adsorption, whereas high concentrations solubilised the dyes and kept them in solution. Basic dye adsorption was increased at high pH values and the opposite was true for the anionic dyes.

Microbial biomass is inexpensive and is known to bind dyes yet of the thousands of diverse species of microorganisms that exist very few have been tested for their potential for biosorption [136]. Other work has shown decolourisation of wastewater by dye degrading organisms such as the white rot fungi *Phanerochete chrysosporium* [137, 138] or certain *Basidiomycete* fungi [139]. In addition *Rhodococcus spp.*, *Bacillus cereus*, and *Plesiomonas achromobacter* have been shown to degrade soluble dyes, acid dye and five azo dyes, respectively [140]. These examples also serve to illustrate another issue in dye effluent treatment by biomass, i.e., that the dye may not be removed as it is but is in fact degraded to form other molecules which although not necessarily coloured, may still contribute significantly to the COD of an effluent. This is certainly true of the degradative products of azo dyes [141]. A review of the removal of colour from textile wastewater using whole bacterial cells suggests that there is great potential for such treatment systems [142, 168]. Other biomasses such as Aeromonas sp. and Fomitopsis carnea have been used to successfully adsorb reactive and cationic dyes respectively [143, 144]. For this reason initial investigations in the context of *Rhyzopus oryzae* biosorption of dyes have been based on extrapolation of data obtained from studies into humic/fulvic acid biosorption and kraft mill decolourisation [145, 146]. *Rhizopus oryzae* is a fungus which contains chitosan as a major component. *Rhizopus oryzae* contains chitosan as a major cell wall component which can be in the region of 60 % by dry mass, therefore it is likely that dye adsorption by *Rhizopus oryzae* will be by attachment to the amino functions on the chitosan molecules [132]. Juang et al. [20] have shown reactive dye adsorption by chitosan to be 3-6 times greater than adsorption by chitin due to the accessibility of the amino functions in chitosan. The presence of acetyl groups in chitin reduces the ability of dye cations to come into contact with nitrogen-free sites thereby limiting dye attachment.

A fungal biomass derived from *Rhizomucor pusillus* as an adsorbent of colour in effluent from a bleach plant [145]. In their work, Christov et al. [145] report that strong colour adsorption was observed in the first few hours of effluent treatment with 48 % of the colour removed after eight hours. A comparison with other adsorbents indicated the following descending order of adsorption: biomass (51 %) > strong anion exchanger (48 %) > activated carbon (37 %) > chitosan (34 %) > chitin (7 %.) > strong cation exchanger (4 %). Chemisorption was suggested as the likely mechanism for adsorption. The vast variety of chemical compounds makes the interaction of dye and microorganisms very case specific. Generally the presence of groups like -OH, -NO_2, or -N=N- favour adsorption whilst -SO_3H groups do not. These groups are known for their ability to remove metal ions from aqueous solutions, therefore it is likely that the same compounds will impart colour-removing properties to organisms containing them.

The adsorption in materials such as squid (*Logligo vulgaris*) and Sepia (*Sepia officinalis*) pens and Anodonta (*Anodonta cygnea*) shells for adsorption of reactive dyes was reported by Figueiredo et al. [146]. In an attempt to improve the sorbent performance, the materials were demineralised and/or deproteinised. The tests showed that the demineralisation of the Anodonta shell and Sepia pen strongly improved their adsorption of the reactive dye, unlike the direct dye. The deproteination alone or combined with demineralisation led to poorer adsorption capacities than those obtained only by demineralisation. This was attributed to the materials being largely composed of calcium carbonate. The demineralised and deproteinised squid pen had enhanced sorption capacities for both types of dye. Smaller improvements were noted for demineralisation alone. The deproteination is important for the squid material which contains large amounts of proteins.

Cucurbituril, a cyclic polymer of glycoluril and formaldehyde [147-149], has been shown to have a high sorption capacity for various types of textile dyes. Buschmann and Schollmeyer [149] suggest the selectivity of cucurbituril for dyes in textile wastes. Cucurbituril is known to form host-guest complexes with aromatic compounds so this is possibly the mechanism for reactive dye adsorption. Another possible mechanism is based on hydrophobic interactions or the formation of insoluble cucurbituril-dye-cation aggregates since adsorption occurs reasonably fast. The solubility is low in water but is increased in the presence of salts, however in the presence of dyes which are sorbing onto the cucurbituril the solubility is reduced. Divalent ions have a stronger effect than monovalent ones, and larger ions more than smaller. Moderate salt concentrations are shown to improve adsorption and high concentrations will lead to dissolution of the cucurbituril [148]. Because of its solubility, cucurbituril is not feasible as an adsorbent in aqueous systems unless it is incorporated into fixed bed sorption filters [148] or covalently fixed onto a suitable support material [148]. Like many other chemical methods, cost is a major disadvantage.

Wood has been a source of adsorbent material both in its natural and modified state. The sawdust of a soft spruce wood (Sitka spruce) has been used for the adsorption of a basic and an acidic dye from solution, finding the removal cost using wood to be only 1.5 – 8.2 % that of a commercial carbon [150, 151]. The results show that spruce wood does have an affinity for basic dyes rather than acidic dyes, although uptake is much less than for active carbons, peats and lignite.

Morais et al. [152] considered the use of eucalyptus bark to adsorb a reactive black dye. Their findings suggest that the uptake by the bark is about half of that of a commercial activated carbon. They conclude that the adsorption was strongly dependent on initial dye concentration and on the pH of the solution.

Netpradit et al. [153] report on the capacity and mechanism of adsorption of three anionic reactive red dyes by waste metal hydroxide sludge. Metal hydroxide sludge is a waste material from the electroplating industry and contains insoluble metal hydroxides and other calcium and sodium salts. The sludge is a positively charged adsorbent with an adsorption capacity for the dyes of 48-62 mg g^{-1}. It is suggested that the adsorption of anionic reactive dyes by a metal hydroxide is facilitated by the dissociation of the metal hydroxide complex which causes the surface to become positively charged [154]. Presence and the quantity of anions (-SO_3^-) on the dyes is an important factor [153] due to the ion exchange mechanism. The maximum colour removal of Reactive Red 141, 120 and 2 was 98 %, 90 %, and 50 %, respectively and is related to the reduction in the presence of sulphonic groups on the dyes. Optimum adsorption was at the pH_{zpc} of the sludge, i.e. at around 8-9. Other sludges such as chrome sludge have been used for dye adsorption [155].

Eggshell membrane is located on the inner surface of an eggshell. It is a dual membrane composed of fibres of polysaccharides and collagen-like proteins. The membrane demonstrates good adsorption characteristics due to the availability of sites containing substituting groups such as hydroxyl, amine and sulphonic groups with which reactive dyes can react [156]. A comparison between the adsorption by activated carbon and egg shell membrane towards reactive levafix brilliant red E-4BA suggests that egg shell membrane has a higher capacity (80 mg g^{-1-1}) than the carbon (60 mg g^{-1}) [156].

The use of natural and synthetic adsorbents for the removal of colour from effluent has been reviewed in this paper. The use of novel alternative adsorbents has continued to attract attention in the literature because of economic considerations, availability and adsorption efficiency. However there is still a need for more detailed information as to the application of the alternatives to carbon in industrial scale processes and to the economic considerations of the alternative adsorption processes. In particular there is a need for more research into tailoring the manufacture of specific adsorbents for particular applications together with more general adsorbents with wider applications. Significant research remains to be done into the development of economical and environmentally friendly desorption and regeneration processes.

Research indicates that there are many factors of the adsorbent and the adsorbate which can affect the extent and rate of the adsorption process. Dye structure, size and molecular shape together with concentration and charge will all influence uptake. Diffusion of the dye in solution and within the adsorbent structure will be affected by these and other parameters such as pore structure, pH of solution, particle size and temperature to name but a few. Surface chemistry and the distribution of adsorption sites on the surface of the adsorbent play a significant role in the adsorption process. Mixtures of dyes can present particular problems for efficient separation and adsorption processes.

Table 3. Maximum monolayer adsorption capacities of some dyes on various adsorbents.

Adsorbent	Dyes	Approximate uptake (g kg^{-1})	Ref
Diatomite	BB9, RBk129, Reactive golden yellow MI-2RN	190, 300, 150	55
Dolomite	RR158	110	69
Eucalyptus bark	Remazol BB	90	152
Fullers earth	BB3, BR22, AB25	500, 460, 36	157
Fungus	Remazol Black B	286-588	49
Kudzu	RR158	60	104
Kudzu	BB3, BR22, BY21	650, 220, 160	104
Kudzu	AB113	30	106
Lignite	BB3, BR22, BY21	730, 500, 675	86
Lignite	AB277	92	38
Maize cob	Astrazon Blue	160	125
Maize cob	Erionyl Red	48	125
Metal hydroxide sludge	RR2, RR120, RR141	63, 48, 56	153
MDF	BB3, BR22, BY21	115, 120, 110	104
MDF	RR158	16	104
Orange peel	AV 17	20	165
Peanut hulls	BB3, BR22, BY21	400, 130, 150	104
Peanut hulls	RR158	13	104
Peat	BB 69, AB25	184-233, 5-9	166
Peat	BB3, BR22, BY21	600, 390, 700	86
Peat, fly ash	BB 29	54-46	72
Peat, fly ash	AB 29	14-15	72
Peat, bentonite, slag, fly ash	Disperse Red 1	23-50	72
Peat resin	BV14, BG4	375, 350	100
Rhyzopus arrhizus	RBk5	588	49
Rhyzopus oryzae	RR 158	197	132
Rice husk	RB 2	130	27
Sepiolite	RBk5, RR239, RY176	121, 109, 169	83
Silica	Astrazone Blue	25	167
Silica	BB3, BR22, AB25	375, 24, 23	157
Zeolite	Maxilon Schwarz FBL-01 Maxilon Goldgelb GL EC	56 15	15
Zeolite	RBk5, RR239, RY176	61, 111, 89	83

As stated earlier, factors such as pH, temperature, particle size, initial dye concentration and adsorbent mass can influence the rate and extent of dye uptake. Consequently a direct comparison of the adsorbent performance is difficult to undertake. Allen [157] has made a simple economic analysis of dye uptake where there has been some degree of operational control over the experimental conditions using similar conditions and two basic dyes, namely, Basic Red 22 and Basic Blue 3. Isotherms were used to assess the quantity of adsorbent required to remove 1 kg of dye. These quantities have been used as a basis for costing the adsorption process. In this simplified approach, no account has been taken of contact time data, and it was assumed that the adsorbent was saturated with dye. In addition, regeneration costs have been neglected, since very few figures are available [158]. In economic terms the peat appears to be the most economic adsorbent for BB3 closely followed by lignite and pith. For BR22 the maximum sorption capacities are again shown by Fuller's earth and the activated carbons; these are of the order of 500 mg dye per g of sorbent. The results indicate a very similar trend to those of BB3 dye [158].

Results for Acid blue 25 indicate that wood is the most economic adsorbent followed by peat, carbon, pith and Fuller's earth. Despite the fact that activated carbons may exhibit the highest adsorption capacity for dyes in most of the systems studied some natural and cheaper materials such as peat and lignite also have high capacities.

A summary of some adsorbent equilibrium monolayer values for dyes is presented in Tables 2, 3. Again it must be remembered that there is no direct comparison between the experimental conditions in the reported values.

Adsorption processes are modeled using a variety of isotherm models, kinetic models and diffusion models. Many systems can be modeled using a number of the classical isotherms such as Freundlich and Langmuir together with more complex isotherms. Similarly many adsorption processes can be modeled using simple kinetic processes as well as more complex diffusion processes. Again further research is necessary to apply the design and simulation models to larger scale pilot work and not just in the small scale laboratory applications.

REFERENCES

1. M.A.S. Al-Ghouti, Mechanisms and chemistry of dye adsorption on diatomite and modified diatomite, PhD Thesis, Queens University of Belfast, 2004.
2. The Colour Index International, 4th ed., Soc. Dyers, Colorists, 2002.
3. T. Robinson, G. McMullan, R. Marchant, P. Nigam, Biores. Technol., **77**, 2001, 247-255.
4. J.R. Easton, Colour in dyehouse effluent, Ed. P. Cooper, Soc. Dyers, Colorists, The Alden Press, Oxford, 1995.
5. C. O'Neill, F.R. Hawkes, D.L. Hawkes, N.D. Lourenco, H.M. Pinheiro, W.J. Delee, J. Chem. Technol. Biotechnol., **74**, 1999, 1009-1018.
6. M.C. Bonneau, J. Chem. Educ., **72**, 1995, 724-725.
7. A.F. Strickland, W.C. Perkins, Textile chemist and colourist, **27**, 1995, 5, 11-15.
8. J. Pierce, J. Soc. Dyers. Colour., **110**, 1994, 131-133.
9. Y.M. Slokar, M. Le Marechal, Dyes. Pigments, **37**, 1998, 335-357.
10. K.K.H. Choy, G. McKay, J.F. Porter, Resour. Conserv. Rec., **27**, 1999, 57-71.
11. D.M. Ruthven, Principles of adsorption and adsorption processes, Wiley-Int., 1984.
12. M. Suzuki, Wat. Sci. Tech., **35**, 7, 1997, 1-11.
13. M. Suzuki, Adsorption engineering, Elsevier, Amsterdam, 1990.
14. R. Rajagopal, Colourage, **38**, 1, 1991, 50-52.
15. V. Meshko, L. Markovska, M. Mincheva, A.E. Rodrigues, Wat. Res., **35**, 2001, 3357-3366.
16. G.M. Walker, L.R. Weatherley, Wat.Res., **33**, 1999, 1895-1899.
17. G.M. Walker, L.R. Weatherley, Wat.Res., **31**, 1997, 2093-2101.
18. G. McKay, J. Chem. Technol. Biotechnol., **32**, 1982, 759-773.
19. Y. Al-Degs, M.A.M. Khraisheh, S.J. Allen, M.N. Ahmad, Wat. Res., **34**, 2000, 927-935.
20. R.S. Juang, R.L. Tseng, F.C. Wu, S.H. Lee, J. Chem. Technol. Biotechnol., **70**, 1997, 391-399.
21. G.L. Rorrer, T.Y. Hsien, J.D. Way, Ind. Eng. Chem. Res., **32**, 1993, 2170-2178.
22. J. Shore, Ind. J. Fibre. Text. Res., **21**, 1996, 1-29.
23. S.J. Allen, K.J.H. Khader, G. McKay, Environ. Pollut., **52**, 1988, 39-53.
24. J.S. Noh, J.A. Schwarz, J. Colloid. Interface. Sci., **130**, 1989, 157-164.
25. C.P. Huang, F.B. Ostovic, J. Environ. Eng. Div., 5, 1978, 863-878.
26. C.A. Leon, L.R. Radovic, Chemistry and physics of carbon, Marcel Dekker, New York, 1994.
27. B.R. Puri, Chemistry and physics of carbon, Marcel Dekker, New York, 1994.
28. G.A. Parks, Chem. Revs., **65**, 1965, 177-198.
29. C.A. Leon, J.M. Solar, V. Calemma, L.R. Radovic, Carbon, **30**, 1992, 797-811.
30. C.P. Huang, M.H. Wu, Wat. Res., 11, 1977, 673-679.
31. C. Moreno-Castilla, F. Carrasco-Marin, A. Mueden, Carbon, **35**, 1997, 1619-1626.
32. J.S. Mattson, H.B. Mark, Activated carbon surface chemistry and adsorption from solution, Marcel Dekker, New York, 1971.
33. A.R. Shawwa, D.W. Smith, D.C. Sego, Wat. Res., **35**, 2001, 745-749.
34. K. Kadirvelu, M. Palanival, R. Kalpana, S. Rajeswari, Biores.Technol., **74**, 2000, 263-265.
35. S.J.T. Pollard, G.D. Fowler, C.J. Sollars, R. Perry, Sci. Tot. Environ., **116**, 1992, 31-52.
36. O. Duggan, Preparation, characterisation and regeneration of activated carbons from Northern Irish lignite, PhD Thesis, Queens University of Belfast, 1998.
37. Y. Al-Degs, Adsorption of anionic reactive dyes on activated carbon from aqueous solution, PhD Thesis, Queens University of Belfast, 2000.
38. G. Walker, Industrial Wastewater Treatment Using Biological Activated Carbon, PhD Thesis, The Queen's University of Belfast, 1995.
39. S.J. Allen, O. Duggan, Wat. Sci. Technol., **35**, 1997, 21-27.
40. S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, Wat. Res., **33**, 1999, 2469-2479.
41. C.H. Giles, A.S.A. Hassan, J. Soc. Dyers. Colourists, **74**, 1958, 846-857.
42. A. Bousher, X. Shen, R.G.J. Edyvean, Wat. Res., **31**, 1997, 2084-2092.
43. G. McKay, H.S. Blair, J. Gardner, J. App. Polym.

Sci., **27**, 1982, 3043-3057.
44. G. McKay, H.S. Blair, J. Gardner, J. App. Polym. Sci., **27**, 1982, 4251-4261.
45. G. McKay, H.S. Blair, J. Gardner, J. App. Polym. Sci., **27**, 1982, 1767-1778.
46. G. McKay, H.S. Blair, J. Gardner, J. App. Polym. Sci., **29**, 1984, 1499-1514.
47. M.S. Chiou, P.Y. Ho, H.Y. Li, Dyes. Pigments, **60**, 2004, 69-84.
48. Z. Aksu, Biochem. Eng. J., 7, 2001, 79-84.
49. Z. Aksu, S. Tezer, Proc. Biochem., **36**, 2000, 431-439.
50. O.A.C. Monteiro Jr, C. Airoldi, J. Coll. Interf. Sci., **212**, 1999, 212-219.
51. F.C. Wu, R.L. Tseng, R.S. Juang, Wat. Res., **35**, 2001, 613-618.
52. Y.C. Wong, Y.S. Szeto, W.H. Cheung, G. McKay, Proc. Biochem., **39**, 2004, 695-704.
53. L.S. Closceri, R.R. Drussels, R.E. Grenderck, American Standard method for water analysis, 17th ed., Washington, 1989.
54. Y. Al-Degs, M.A.M. Khraisheh, M.F. Tutunji, Wat. Res., **35**, 2001, 3724-3728.
55. M. Al-Ghouti, M.A.M. Khraisheh, S.J. Allen, M.N. Ahmad, J. Environ. Manag., **69**, 2003, 229-238.
56. W. Stumm, J.J. Morgan, Aquatic chemistry, 3rd ed., Wiley, New York, 1995.
57. J.P. Chen, M. Lin, Wat. Res., **35**, 2001, 2385-2394.
58. L. Benefield, B. Weand, Process chemistry for water and wastewater treatment, Prentice-Hall, USA, 1982.
59. G. Rytwo, D. Tropp, C. Serban, App. Clay. Sci., **20**, 2002, 273-282.
60. G. McKay, M.S. Otterburn, A.G. Sweeney, Wat. Res., **15**, 1981, 327-331.
61. G. McKay, M.S. Otterburn, A.G. Sweeney, Wat. Res., **14**, 1980, 15-20.
62. G. McKay, F. Alexander, Chem. Eng., 4, **1977**, 243-244.
63. S.A. Wasay, M.J. Haron, S. Tokunaga, Wat. Environ. Res., **68**, 1996, 295-300.
64. A.G.S. Prado, B.S. Miranda, G.V.M. Jacintho, Surf. Sci., **545**, 2003, 276-282.
65. A.S. Koparal, Y. Yavuz, U.B. Ogutveren, Wat. Environ. Res., **74**, 2002, 521-525.
66. J.A. Thomas, J.M. Longo, Chem. Geol., **109**, 1993, 201-213.
67. P. Brady, J. Krumhansl, H. Papenguth, Geochim. Cosmochim. Acta, **60**, 1996, 727-731.
68. P. Staszczuk, E. Stefaniak, B. Bilinski, E. Szmanski, R. Dobrowolski, S.A. Jayaweera, Powd. Technol., **92**, 1997, 253-257.
69. G. Walker, L. Hansen, J.A. Hanna, S.J. Allen, Wat. Res., **37**, 2003, 2081-2089.
70. G. Atun, G. Hisarli, W.S. Sheldrick, M. Muhler, J. Coll. Interf. Sci., **261**, 2003, 32-39.
71. S. Kacha, Z. Derriche, S. Elmaleh, Wat. Environ. Res., **75**, 2003, 15-20.
72. K. Ramakhrishna, T. Viraraghavan, Wat. Sci. Technol., **36**, 1997, 189-196.
73. S. Al-Asheh, F. Banat, L. Abu-Aitah, Adsorpt. Sci. Technol., **21**, 2003, 451-461.
74. M. Borisover, E. Graber, F. Bercovich, Z. Gerstl, Chemosphere, **44**, 2001, 1033-1040.
75. G. Alther, Removal of oil from water with organoclays, Ferndale, MI. Biomin. Inc. 810/544-2552, 1998.
76. C. Kim, M. Hosomi, A. Murakami, M. Okada, Wat. Sci. Technol., **30**, 1994, 159-167.
77. S. Panpanit, C. Visvanathan, J. Membr. Sci., **184**, 2001, 59-68.
78. N. Al-Bastaki, F. Banat, *Res. Conserv. Recycl.*, **41**, 2004, 103-113.
79. S. Kacha, M.S. Ouali, S. Elmaleh, Rev. Sci. Eau, 2, 1997, 233.
80. L. Bergaoui, J.F. Lambert, H. Suquet, M. Che, J. Chim. Phys., **92**, 1995, 1486.
81. F.B. Dilek, S. Bese, Wat. SA, 27, 2001, 361-366.
82. N.K. Lazaridis, T.D. Karapantsios, D. Georgantas, Wat. Res., **37**, 2003, 3023-3033.
83. O. Ozdemir, B. Armagan, M. Turan, M.S. Celik, Dyes. Pigments, **62**, 2004, 49-60.
84. I. Belkevich, K.A. Gayduk, L.R. Christova, Proc. 5th Int. Peat. Congr., 1, 1976, 328.
85. M.E. Leslie, Am. Dyest. Rep., **63**, 1974, 15-18.
86. M.A. Murray, Adsorption and desorption of basic dyes in the aqueous phase, PhD Thesis, Queens University of Belfast, 1995.
87. K.Y.H. Khader, Adsorption of basic dyes using peat and lignite, PhD Thesis, The Queen's University of Belfast. 1988.
88. S.J. Allen, Mathematical modelling of the adsorption of dyes from effluent using peat, PhD Thesis, Queens University of Belfast, 1981.
89. J. Dufort, M. Ruel, Proc. 4th Int. Peat Cong., Otanieni, Finland., 1972, 299.
90. G. McKay, V.J.P. Poots, J. Chem. Technol. Biotechnol., **30**, 1980, 279-292.
91. G. McKay, M. El-Geundi, M.M. Nassar, Wat. Res.,

22, 1988, 1527-1533.
92. G. McKay, G. Ramprasand, P. Mowli, Wat. Res., **21**, 1987, 375-377.
93. L.H. Ong, V.E. Swanson, Econ. Geol., **61**, 1966, 1214-1231.
94. S.J. Allen, G. McKay, K.Y.H. Khader, J. Coll. Interf. Sci., **126**, 1988, 517-524.
95. S.J. Allen, G. McKay, K.Y.H. Khader, Environ. Pollut., **56**, 1989, 39-50.
96. S.J. Allen, G. McKay, K.Y.H. Khader, J. Chem. Technol. Biotechnol., **45**, 1989, 291-302.
97. S.J. Allen, P.A. Brown, M.A.; Murray, O. Flynn, J. Res. Cons. Recyc., 11, 1994, 25-39.
98. S.J. Allen, M.A. Murray, Dirasat., **22**, 1995, 423-443.
99. S.J. Allen, L.J. Whitten, M.A. Murray, O.P. Duggan, P.A. Brown, J. Chem. Technol. Biotechnol., **68**, 1997, 442-452.
100. Q. Sun, L. Yang, Wat. Res., **37**, 2003, 1535-1544.
101. A. Gaines, Lignite: A down to earth fuel, Public Lecture, Queens University Belfast, 1984.
102. S.V. Mohan, N.C. Rao, J. Karthikeyan, J. Haz. Mat., **90**, 2002, 189-204.
103. S. Clark, P. Brown, R. Pitt, Proc. Wat. Environ. Fed. Industr. Waste Conference, 2000, St. Louis, USA.
104. R. Matthews, The adsorption of dyes using kudzu, peanut hulls and MDF sawdust, PhD Thesis, Queens University of Belfast, 2003.
105. S.J. Allen, Q. Gan, R. Matthews, P.A. Johnston, Biores. Technol., **88**, 2003, 143-152.
106. B. Koumanova, B. Achova, S.J. Allen, J. Univ. Chem. Technol. Metal. (Sofia), **38**, 2003, 735-746.
107. A. Nag, Trans. IChemE., **73**, 1995, 299-304.
108. G. Malmary, F. Perineau, J. Molinier, A. Gaset, J. Chem. Technol. Biotechnol., **35**, 1985, 431-437.
109. F. Perineau, J. Molinier, A. Gaset, J. Chem. Technol. Biotechnol., **32**, 1982, 749-758.
110. K.S. Low, C.K. Lee, Biores. Technol., **61**, 1997, 121-125.
111. Rajeshwarisivaraj, S. Sivakumar, P. Senthilkumar, V. Subburam, Biores. Technol., **80**, 2001, 233-235.
112. R.M. Liversidge, G.J. Lloyd, D.A.J.; Wase, C.F. Forster, Process Biochem., **32**, 1997, 473-477.
113. G. Sun, X. Xu, Ind. Eng. Chem. Res., **36**, 1997, 808-812.
114. C. Namasivayam, D. Prabha, M. Kumutha, Biores. Technol., **64**, 1998, 77-79.
115. C. Namasivayam, N. Kanchana, R.Y. Yamuna, Waste. Manag., 13, **1993**, 89-95.
116. G. Annadurai, R.S. Juang, D.J. Lee, J. Hazard. Mater., **92**, 2002, 263-274.
117. C. Namasivayam, N. Muniasamy, K. Gayatri, M. Rani, K. Ranganathan, Biores. Technol., **57**, 1996, 37-43.
118. G. McKay, M.S. Otterburn, J.A. Aga, Wat. Air. Soil. Pollut., **24**, 1985, 307-322.
119. E. Longhinotti, F. Pozza, L. Furlan, M. Sanchez, M. Klug, M.C.M. Laranjeira, V.T. Favere, J. Braz. Chem. Soc., 9, 1998, 435-440.
120. L.C. Morais, O.M. Freitas, E.P. Goncalves, L.T. Vasconcelos, C.G. Gonzalez Beca, Wat. Res., **33**, 1999, 979-988.
121. V.J.P. Poots, G. McKay, J.J. Healy, Wat. Res., **10**, 1976, 1067-1070.
122. H.M. Asfour, O.A. Fadali, M.M. Nassar, M.S. El-Geundi, J. Chem. Technol. Biotechnol., **35**, 1985, 21-27.
123. H.M. Asfour, M.M.; Nassar, O.A. Fadali, M.S. El-Geundi, J. Chem. Technol. Biotechnol., **35**, 1985, 28-35.
124. M.M. Nassar, M.S. El-Geundi, J. Chem. Technol. Biotechnol., **50**, 1991, 257.
125. M.S. El-Geundi, Wat. Res., **25**, 1991, 271-273.
126. C. Namasivayam, R.T. Yamuna, J. Chem. Technol. Biotechnol., **53**, 1992, 153-157.
127. K.S. Low, C.K. Lee, K.K. Tan, Biores. Technol., **52**, 1995, 79-83
128. C. Namasivayam, D.J.S.E. Arasi, Chemosphere, **34**, 1997, 401-417.
129. S.K. Khare, K.K. Panday, R.M. Srivastava, V.M. Singh, J. Chem. Technol. Biotechnol., **38**, 1987, 99-104.
130. G.S. Gupta, G. Prasad, V.N. Singh, Wat. Res., **24**, 1990, 45-50.
131. L.M. Turemen, Investigation of the adsorption of reactive dyes and heavy metal ions from synthetic textile effluent by eggshell membrane, PhD Thesis, Queens University of Belfast, 2001.
132. K.A. Gallaher, Mass transfer and biosorption processes with Rhizopuz oryzae as an adsorbent of reactive dye and metal ions from aqueous effluent, PhD Thesis, Queens University of Belfast, 1998.
133. K.G. Bhattacharyya, A. Sarma, Dyes. Pigments, **57**, 2003, 211-222.
134. A.K. Jain, V.K. Gupta, A. Bhatnagar, Suhas, J. Haz. Mat., **101**, 2003, 31-42.
135. P. Janos, H. Buchtova, M. Ryznarova, Wat. Res., 2003, 4938-4944.
136. J.K. Polman, C.R. Breckenridge, Text. Chem.

Colour., April, 1996, 31-35.
137. W.L. Chae, S.L. Lee, World J. of Microbiol. Biotech., **10**, 5, 1994, 556-559.
138. L. Chung, K. Stevens, Env. Toxicol. Chemistry, **12**, 11, 1993, 2121-2132.
139. J.S. Knapp, P.S. Newby, L.B. Reece, Enz. Microbial Tech., 17, **1995**, 664-668.
140. K.A. Croft, B.R. Kim, J. Wat. Pollut. Cont. Fed., **61**, 6, 1982, 872-879.
141. T. Zimmerman, H.G. Kulla, T. Leisinger, Eur. J. Biochem., **129**, 1982, 197-203.
142. C.I. Pearce, J.R. Lloyd, J.T. Guthrie, Dyes Pigments, **58**, 2003, 179-196.
143. T.L.Hu, Wat. Sci. Tech., **26**, 1992, 357-366.
144. A.K. Mittal, S.K. Gupta, Wat. Sci. Tech., **34**, 10, 1996, 81-87.
145. L.P. Christov, B. van Driessel, C.A. du Plessis, Proc. Biochem., **35**, 1999, 91-95.
146. S.A. Figueiredo, R.A. Boaventura, J.M. Loureiro, Separ. Purif. Technol., **20**, 2000, 129-141.
147. S. Karcher, A. Kornmuller, M. Jekel, Wat. Sci. Technol., **40**, 1999, 425-433.
148. S. Karcher, A. Kornmuller, M. Jekel, Wat. Res., **36**, 2002, 4717-4724.
149. H.J. Buschmann, E. Schollmeyer, Textilveredelung, **29**, 1994, 58-60.
150. G. McKay, I.F. McConvey, J. Chem. Technol. Biotechnol., **31**, 1981, 401-408.
151. G. McKay, I.F. McConvey, Chem. Eng. Proc., **19**, **1**985, 285-295.
152. L.C. Morais, O.M. Freitas, E.P. Goncalves, L.T. Vasconcelus, C.G. Gozalez Beca, Wat. Res., **33**, 1999, 979-988.
153. S. Netpradit, P. Thiravetyan, S. Towprayoon, Wat. Res., **37**, 2003, 763-772.
154. K.R. Ramakrishna, T. Viraraghavan, Wat. Sci. Technol., **36**, 2, 1997, 189-196.
155. C.K. Lee, K.S. Low. S.W. Chow, Environ. Technol., **17**, 1996, 1023-1028.
156. M. Wolki, S.J. Allen, P.A. Ulbig, Chem. Technik, **51**, 1999, 321-325.
157. S.J. Allen, Types of adsorbent materials, in: G. McKay, Ed., Use of adsorbents for the removal of pollutants from wastewater, CRC, Boca Raton, USA, 1996, 59.
158. G. McKay, Chem. Eng. J., **27**, 1983, 187-196.
159. W.T. Tsai, C.Y. Chang, M.C. Lin, S.F. Chien, H.F. Sun, M.F. Hsieh, Chemosphere, **45**, 2001, 51-58.
160. C. Namasivayam, D. Kavitha, Dyes. Pigments, **54**, 2002, 47-58.
161. G. McKay, H.S. Blair, J.R. Gardner, J. Colloid. Interface. Sci., **95**, 1983, 108-119.
162. M.S. Chiou, H.Y. Li, J. Hazard. Mater., **93**, 2002, 233-248.
163. H. Yoshida, A. Okamoto, T. Kataoka, Chem. Eng. Sci., **48**, 1993, 2267-2272.
164. F.C. Wu, R.L. Tseng, R.S. Juang, J. Hazard. Mater., **73**, 2000, 63-75.
165. R. Sivaraj, C. Namasivayam, K. Kadirvelu, Waste. Manag., **21**, 2001, 105-110
166. Y.S. Ho, G. McKay, Chem. Eng. J., **70**, 1998, 115-124.
167. G. McKay, A. I. Chem. Eng. J., **30**, 1984, 692-697.
168. T.L. Hu, Wat. Sci. Technol., **34**, 10, 1996, 89-95.
169. D. Pishev, S. Veleva, A. Georgieva, J.Univ. Chem. Technol. Met. (Sofia), **39**, 3, 2004, 317-326.
170. K.Dimov, E. Terlemezyan, D. Dimitrov, Tekstilna promishlenost, 2, 1981, 71-73, (in Bulgarian).
171. B. Koumanova, B. Achova, S.J. Allen, Intern. J. Env. Poll., (in press).