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Biosorption of Copper from Waste Waters: A Review

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BIOSORPTION OF COPPER FROM WASTE WATERS: A REVIEW

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ABSTRACTS

A comprehensive literature review has been carried out on the sorption of copper ions onto various biosorbents. Extensive research has been carried out using peat as a sorbent and the sorption capacity of copper on different peats varies by a factor of over fifty. Furthermore, this paper identifies that copper sorption capacities have been reported for over thirty other different biosorbents. The paper reviews the capacities of the various biosorbents for copper and discusses the range of kinetic mechanisms used by different researches to correlate kinetic experimental data. The suitability of the various kinetic models for the sorption of copper from wastewaters onto different biosorbents is discussed.

The review identifies several deficiencies in the literature. Many of the studies on equilibrium isotherms only apply one method of analysis. Researchers fail to test experimental equilibrium date using several models and do not determine the best fit model by error analysis or by postulating a sorption mechanism. The same criticism is valid for kinetic studies. The application of more than one kinetic model is extremely rare. Another major problem arises in the characterisation of adsorbent materials, since very little information is provided on surface area, pore size distribution, surface activity, particle size, hardness or attrition rates and influence of pH. These are key factors in developing and designing wastewater treatment systems.

Key words: Biosorbents, Peat, Copper, Sorption.

1. INTRODUCTION

Adsorption is an effective separation process for a wide variety of applications. It is now recognised as an effective and economic method for the removal of pollutants from wastewaters. The most widely used adsorbent is activated carbon but in the past ten years considerable attention has been directed towards low cost biosorbents because activated carbon is expensive, an alternative inexpensive adsorbent could drastically reduce the cost of an adsorption system. Many waste or naturally occurring materials have been investigated to assess their suitability for application the field of water pollution control. The use of low-cost natural materials for the removal of copper, include peat[1-17], anaerobically digested sludge[18], kaolin, illite and montmorillonite clay[19], treated bagasse, treated acacia bark, treated laurel bark and treated techtona bark[20], fly ash[21], *Penicillium spinulosum*[22], rice hulls, dyestuff-treated (Red) rice hulls and dyestuff-treated (Yellow) rice hulls[23], resins[24], moss *Calymperes delessertii Besch*[25], water hyacinth[26](*Eichornia crassipes), Rhizopus arrhizus*, *Cladosporium resinae* and *Penicillium italicum*[27], tea leaves[28], amorphous iron hydroxide[29], activated carbon[30], chitin[31], Viable *S. cerevisiae*, Ethanol-killed *S. cerevisiae* and Heat-killed *S. cerevisiae*[32], sawdust[33], bottom ash[34], sludge solid[35], *Aspergillus oryzae*, *Rhizopus oryzae*, *Aspergillus oryzae* and treated *Aspergillus oryzae*[36], *Chlorella vulgaris* and *Zoogloea ramigera*[37], oil-palm fibres, dye-treated oil-palm fibre and natural oil-palm fibre[38], chitosan[39], Transport studies for the sorption of copper ions by *G. lucidum*, treated *G. lucidum*, treated *A. niger* and treated Sludge[40], goethite[41], dried water hyacinth roots[42], yeast biomass and yeast cell walls[43], ricebran[44], formaldehyde-crosslinked seaweed biomass[45], activated carbons obtained from apricot stones, coconut shells, and lignite coal[46], kaolinite[47,48], *Zoogloea ramigera*[49], *Saccharomyces cerevisiae*[50], banana pith[51], *Phormidium laminosum* biomass[52], coconut husk, coconut husk treated with CHRY, CHAB9 and CHAB5[53], *Sargassum fluitans* biomass[54], lignite[55], chemically-reinforced biomass of marine algae[56], shea butter (Butyrospermum-Parkii) seed husks[57], *Ascophyllum nodosum* seaweed diomass[58], Congo Red-Attached poly(EGDMA-HEMA) microbeads[59], blast furnace sludge[60], rice bran, soybean and cottonseed hulls[61], palm pressed fibers[62], goethite[63], coconut coir[64], peanut hull carbon and granular activated carbon[65], granular activated carbon (GAG) and biosorbents: *Saccaromyces cerevisiae* yeast (caustic treated and active) immobilized in GAG; Yeast (caustic treated) immobilized in alginate acid, and alginate itself[66], immobilized bimomass[67,68], silica gel, activated carbon, kieselguhr and kaolin, Zeolites ZSM-5 and Y, bentonite, diatomite, fly ash, saw dust and residual ash from the food industry[69], activated carbon[70] and coirpith carbon[71] have been reported.

During the last three decades, peat has been the subject of numerous studies which have focused on environmental pollution control. It has been demonstrated to be effective in the removal of oil[72], BOD/COD in slaughterhouse wastes[73], heavy metals[3], nutrients[74], dyes in textile effluents[75], pesticides from agricultural land drainage[76] and trace organics from industrial effluents[77].

The present paper reviews and summarizes the major findings for the sorption of copper ions from wastewaters onto a wide variety of biosorbents. The key objectivies of this paper are :

- to identify the wide range of biosorbents capable of removing metal ions from wastewaters;
- to compare the equilibrium capacities of these biosorbents for copper ions;
- to discuss the mechanisms of copper sorption onto biosorption;
- to review the kinetics of copper ion sorption.

2. DISCUSSION

2.1 General

Early reports refer to substantial reductions in metal content when aqueous wastes were run through peat bogs[78], though the precise extent of metal ion reduction and the life time of the sorbent were not well documented and almost certainly not understood. Further reports of the biosorption of metals have continued to this day and currently, recycling waste bio-materials is considered environmentally sound practice and is supported by public opinion and government policy. In less well-developed countries, governments and commerce are expanding their industries, often with serious accompanying pollution. Even well-developed countries have their share of leachates from established waste tips, acid mine drainage and industrial wastewaters[11]. Systems where the biosorption of copper and other metal ions occurs include : in conventional secondary wastewater treatment plants (activated sludge and biofilm), in natural and artificial wetlands for stormwater and tertiary polishing, AMD treatment and industrial waste treatment – particular in the electroplating and microelectronics industries where film-forming polymers, stabilizers, photo-sensitive polymers and etching chemicals form a source of biosorbent chemicals. The number of literature reports on the removal of metals ion by sorption and biosorption has risen sharply particularly during the past fifteen years. The methods utilised, the metals sorbed and the materials used for copper sorption are diverse, which in turn, makes comparisons difficult. Over fifty papers have been published in the 1990's on the specific topic of copper sorption and there has been no significant attempt to review and compare the data.

2.2 Copper Sorption Capacities onto Various Biosorbents

The sorption of copper ions from aqueous systems has been reported for over thirty different biosorbents as shown in Table 1. The most prolific sorbent tested is peat in its various forms of sphagnum moss, eutrophic, oligotrophic and acid treated material. A wide range of capacities for copper ions is observed. In general for sorption capacities of greater than 30 mg copper ion/g peat the material has been acid treated. For the eutrophic sphagnum moss peats, the capacities are mostly in the range 10 – 30 mg/g whereas the oligotrophic peats are mostly 1 - 15 mg/g. Activated carbons generally show a relatively a low sorption capacity, around 10 mg/g, although a peanut hull based activated carbon[65] has a capacity of 65.6 mg/g. Table 1 indicates a number of hulls have been used directly for copper removal including soybean, cotton seed, rice bran and coconut husk with wide ranging copper sorption values of 38.8, 19.1, 76.9 and 3.1 respectively. Several natural biosorbents having a significant cellulose structure have been tested, namely coconut coir, coirpith carbon, oil palm fibre, banana pith, lignite and sawdust and have the following copper sorption capacities 227, 39.7, 2.0, 13.5, 2.6 *and sawdust respectively. The capacity of 227 mg copper/g using coconut coir is the* highest reported literature sorption capacity for copper. A wide variety of microbial biomasses and treated biomasses have been used for copper sorption. Almost twenty are listed and vary in capacity from 129 mg/g for immobilised *sargassum fluitans* to 1.1

Table 1. The Langmuir Equilibrium Sorption Capacities for Sorption of Copper by Different Sorbents.

Isotherm - Dubinin-Radush kevich=DR, F=Freundlich, L=Langmuir, RP=Redlich-Peterson, T=Temkin & BET=(Brunauer-Emmett-Teller)
Kinetics - FO=first order; Mechanism - IE=Ion exchange; E=Elovich & D=diffusion or mass transfer; Mechanism - IE=Ion exchange

X_m (mg/g)	Material	Reference	Isotherm	Kinetics	Column	Mechanism	pH	Temp. (°C)	Particle Size
227	Modified coconut coir	Baes *et al*[64]	L (F, DR)		N	IE	6	25	
222	Chitosan	McKay *et al*[128]	L		N				710-1000um
152	Biosorbent – *Bacillus subtilis*@	Beveridge[129] and Brierley and Brierley[130]			N			30	
149	Chitosan in ammonium nitrate	Inoue *et at*[103]			N			30	
146	Bacter. cell walls prep. – *Bacillus subtillis*	Beveridge[129]			N				
129	*Marine algae - Sargassum fluitans*, PEI	Leusch *et al*[131]	L (F, DR)		N		3.5	25	0.841-1.00mm
125.1	Chitosan – crosslinked (Cu)	Inoue *et al*[103]			N			30	
95.46	Chitosan – PSC resin	Kondo *et al*[102]	L		N			25	100-120 mesh

@ Biomass is not necessarily in its natural state.

X_m (mg/g)	Material	Reference	Isotherm	Kinetics	Column	Mechanism	pH	Temp. (°C)	Particle Size
98.69	Chitin derivative	Tikhonov *et al*[106]			N				
91	*Marine algae – Ascophyllum nodosum* , FA	Leusch *et al*[56]	L (F, DR)		N		3.5	25	0.841-1.00 mm
88.37	Chitosan - PT - resin	Inoue *et al*[103]			N			30	
83.85	Chitosan – PEI	Yoshida *et al*[132]	L		N			25	
80	Yeast – *Candi da tropicalis*	Mattuschka *et al*[133]	L (F)		N			30	
76.9	Rice bran	Marshall *et al*[134]	L		N		5-8	20	
76	Biosorbent - *Fungal biomass*	Beveridge[129]			N				
65.6	Activated carbon peanut hull	Periasamy & Namasivayam[65]	L	FO	N	IE	5	30	0.575mm
64.5	Activated digested sludge	Rao *et al*[41]	F (L)		N		5	25	100um
65.38	Chitosan – WA30	Yoshida *et al*[132]	L		N				
61.9	Peat (Ireland) - acid treated	Smith *et al*[5]			Y	IE			
61.28	Chitosan – CLC resin	Kondo *et al*[107]	L		N				
56.8	Chitosan	Findon *et al*[39]			N				
>52.4	Peat (Ireland) - acid treated	Smith *et al*[4]			N	IE			

(continued)

Table 1. Continued.

X_m (mg/g)	Material	Reference	Isotherm	Kinetics	Column	Mechanism	pH	Temp. (°C)	Particle Size
52.3	*Activated sludge – Zoogloea ramigera*	Sag & Kutsal[49]	L		N		4.0	45	
50	*Manganese-oxidizing bacteria*	Stuetz *et al*[135]			N				
49.0	Anaerobically digested sludge	Gould & Genetelli[18]	L (F, T)		N		5-8	25	
42.6	Moss – *Calymperes delessertii Besch*	Low & Lee[25]	L		Y	IE			
40	Chitosan – prawn shell	Findo *et al*[39]	L		N				
39.7	Coirpith carbon	Namasivayam & Kadirvelu[71]	L (F)	FO	N	IE	4.2	25	200-500um
38.8	Soybean hulls	Marshall & Champagne[136]	L		N		4-5		<2mm
38.7	Peat (Muthurajawela) - acid treated	Dissanayake & Weerasooriya[9]			N		1-6		120 mesh

CHRY: Coconut husk treated with Reactive Yellow 2 (CI 18972); CHAB9: Coconut husk treated with Acid Blue 29 (CI 20460)
CHAB5: Coconut husk treated with Acid Blue 25 (CI 62055); FA: Marine algae were crosslinked with formaldehyde; PEI: Marine algae were embedded in polyethylene imine

X_m (mg/g)	Material	Reference	Isotherm	Kinetics	Column	Mechanism	pH	Temp (°C)	Particle Size
32.1	Fungi – *Rhizopus arrhizus*	Zhou *et al*[137]	L (F)		Y	IE	7	25	
32	Bacter. cell walls prep. – *Bacillus licheniformis*	Beveridge[129]			N				
28.5	Activated sludge – *Ganoderma lucidum*	Roa *et al*[40]	L (F)		N		5	25	100um
28.5	Activated sludge - *Asperigillus niger*	Rao *et al*[40]	L (F)		N		5	25	100um
27.1	Moss – *Calymperes delesserttii Besch*	Lee & Low[12]	L		Y	IE		0-60	200-1700um
23.6	Blast furnace sludge	López *et. al*[60]	L (F)		N			20	
23.3	Montmorillonite clay	Farrah *et al*[19]	L		N			25	< 2um
23.0	Sphagnum moss peat	McLellan & Rock[11]	L, F		Y				
22.58	*Ascophyllum nodosum*	De Carvalho *et al*[138]					4.5	22-25	
20.9	Dried water hyacinth roots - *Eichhoria crassipes*	Low *et al*[42]	L		N	IE	5.1 - 5.4	25	1mm
20.0	Moss peat – agricultural use	Aho & Tummavuori[8]			N				
19.6	Eutrophic moss peat - acid treated	Chen *et al*[13]	L (F)		N	IE	2.5 - 4.2		

(continued)

Table 1. Continued.

X_m (mg/g)	Material	Reference	Isotherm	Kinetics	Column	Mechanism	pH	Temp (°C)	Particle Size
19.1	Cottonseed hulls	Marshall & Champagne[134]	L		N		2-5		<2mm
18.5	Sphagnum peat	Viraraghavan & Dronamraju[15]	L (F)		N		2-9	5-21	
18.0	Sphagnum moss peat	McKay *et al*[139]	L (F, RP)		N		4.5	20	500-710um
18	Fungus – *Cladosporium resinae*	Gadd *et al*[140]	L (F, BET)		N		5.5	20	10-400um
17.8	Peat (Ireland)	Smith *et al*[5]			Y		5		1.0-0.5mm
17.6	Sphagnum moss peat	Allen *et al*[14]	L (F, RP)	D	N				
17-40	Yeast – *Saccharomyces cerevisiae*	Volesky and May-Phillips[50]			N		4-5	25	
16.5	Peat - acid treated	Bunzl *et al*[2]			N	IE		25	0.2-0.78mm
16.4	Sphagnum moss peat – Ireland	Ho *et al*[16]			N				
16	Fungus – *Rhizopus arrhizus*	Tobin *et al*[141]	L		N			25	
15.9	Dye-treated oil-palm fibre	Low *et.* *al*[38]	L		N				1mm

X_m (mg/g)	Material	Reference	Isotherm	Kinetics	Column	Mechanism	pH	Temp (°C)	Particle Size
15	*Rhizopus arrhizus*	Sag & Kutsal[142]	F				4	25	
14.0	Amorphous iron hydroxide	Mustafa & Haq[29]	L		N		7.0	25-70	
13.8	Fungal mycelia – *Aspergillus oryzae*	Huang *et. al*[36]	L		N				
13.5*	Banana pith	Low *et. al*[51]	L		Y		4.5	20	<1mm
12.6	Peat (New Zealand)	McKay *et. al*[143]	L (F, RP)		N			30	500-710um
12.7	Moss peat – energy production	Aho & Tummavuori[8]			N				
12.3	CHRY	Low *et al*[53]			N				
12.1	Eutrophic moss peat	Gosset *et al*[10]			N				0.5-5mm
12.1	Oligotrophic moss peat	Gosset *et al*[10]			N				0.5-5mm
12.1	Fungal mycelia - *Rhizopus oryzae*	Huang *et al*[36]	L		Y		2-9		
11.6	*Fungi- Aspergillus carbonarius*	Al Asheh & Duvnjak[144]	L (F)		N		6		
11.6	Candida utilis	Norris and Kelly[145]			N				
11	Yeast – *Pichia guilliermondii*	Mattuschka *et al*[133]	L, F		N			30	
10.5	Saccharomyces cerevisiae	Norris and Kelly[145]			N				

(continued)

Table 1. Continued.

X_m (mg/g)	Material	Reference	Isotherm	Kinetics	Column	Mechanism	pH	Temp (°C)	Particle Size
10.1	Fungi – treated *Aspergillus niger*	Roa *et al*[40]	L (F)		N		5	25	
10	Peat (UK)	Ong & Swanson[1]			N				<40 mesh
10	Yeast – *Saccharomyces cerevisiae*	Mattuschka *et al*[133]	L, F		N			30	
10	Freshwater alga – *Scenedesmus obliquus*	Mattuschka *et al*[133]	L, F		N			30	
10	Fungus – *Rhizopus arrhizus*	Gadd *et al*[140]	L (F,BET)		N		5.5	20	10-400um
9	Fungus – *Penicillium chrysogenum*	Niu *et al*[146]			N			30	35-50 mesh
9.22	Activated carbon (stone – almond, olive, peach)	Ferro-García *et al*[30]	L		N				0.13-0.49 mm
8.13	CHAB9	Low *et al*[53]			N				
7.75	CHAB5	Low *et al*[53]			N				
>7.5	Peat (Ireland)	Smith *et al*[4]			N				
7.5	*Amaranthus spinosus*	Chen *et al*[147]	L, F	D	Y		5.5 - 5.7	25	

X_m (mg/g)	Material	Reference	Isotherm	Kinetics	Column	Mechanism	pH	Temp. (°C)	Particle Size
6.89	Fungal mycelia - *Rhizopus ooryzae*	Huang *et al*[36]	L		N				
6.41	Oligotrophic peat moss - *acid treated*	Chen *et al*[13]	L (F)		N		3.1 - 3.5		
6.3	Yeast – *Saccharomyces cerevisiae*	Brady and Duncan[148]			Y		7.2	25	
6.06	Fungal mycelia - *Aspergillus oryzae*	Huang *et al*[36]	L		N				
5.90	lignite (USA)	Ong & Swanson[1]			N				
5.1	Peat (Rastunsuo)	Tummavuori & Aho[7]			N	IE			
5	Filament. Bacter. - *Streptomyces noursei*	Mattuschka *et al*[133]			N			30	
5	Bacterium – *Bacillus sp.*	Cotoras *et al*[149]	L		Y			28	
4	*Solanum nigrum*	Chen *et al*[147]	L, F	D	Y		5.5 - 5.7	25	
3.60	Granular activated carbon	Periasamy & Namasivayam[65]	L	FO	N	IE	5		0.575mm

(continued)

Table 1. Continued.

X_m (mg/g)	Material	Reference	Isotherm	Kinetics	Column	Mechanism	pH	Temp. (°C)	Particle Size
3.07	Coconut husk	Low *et al*[53]			N				
2.93	*Rhizopus oryzae*	Huang & Huang[150]	L, F	D	Y		5.5 - 5.7	25	2-3mm
2.6	Peat	Eger *et al*[6]			N				
2.56	Lignite	Allen & Brown[14]	L (F, RP)		N			25	
2.54	Illite clay	Farrah *et al*[19]	L		N				< 2um
1.98	Natural oil-palm fibre	Low *et. al*[38]			N				1mm
1.91	Treated unicellular yeast – *Saccharomyces cerevisiae*	Huang *et al*[32]	L		Y		2-9		
1.74	Sawdust (Bassia Latifolia)	Vaishya & Prasad[33]	L		Y		7.3		499um
1.7	Fungus – *Aspergillus niger*	Townsley *et al*[151]			N		5.5	25	
1.64-1.95	*Aspergillus oryzae* (acid treated)	Huang & Huang[150]							2-3mm
1.46	Ethanol-killed unicellular yeast - *Saccharomyces cerevisiae*	Huang *et. al*[32]	L (F)		Y		2.9	25	
1.40	Kaolin clay	Farrah *et al*[19]	L (F)		N			25	< 2um

X_m (mg/g)	Material	Reference	Isotherm	Kinetics	Column	Mechanism	pH	Temp. (°C)	Particle Size
1.38	Fly ash	Panday *et al*[21]	L		Y		2-9		
1.2	Fungus – *Trichoderma viride*	Townsley *et al*[151]			N		5.5	25	
1.08	Heat-killed unicellular yeast - *Saccharomyces cerevisiae*	Huang *et. al*[32]			N				
< 1	Bituminous coal (USA)	Ong & Swanson[1]			Y				<40 mesh
0.79	*Aspergillus oryzae*	Huang & Huang[150]							2-3mm
0.75	Fungus - *Penicillium chrysogenum*	Paknikar *et al*[152]			N				
0.4-2	Fungus - *Penicillium spinulosum*	Townsley *et al*[151]			N		5.5	25	

mg/g for heat-killed *s. cerevisiae*. In addition, a wide range of minerals, clays, sludges and fly ash have been used with varying degrees of success as shown in Table 1.

2.3 Equilibrium Sorption Models

Equilibrium isotherms are measured to determine the capacity of biosorbents for coppers ions. The biosorbents are usually agitated with fixed volumes of solutions of copper ions of varying concentrations, until equilibrium, that is saturation, has been reached. The relationship between the amount of copper adsorbed and the copper ion concentration remaining in solution is described by an isotherm equation. The three most common types for describing this type of system are the Langmuir (L), Freundlich (F) and the Redlich-Peterson (RP). The isotherms used to describe the systems in the literature have been incorporated into Table 1 using the designated letters L, F and R-P. The mathematical forms of these three isotherm equations are described in the following section.

The Langmuir equation[79] has been used extensively for dilute solutions[80] in the following form,

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \qquad (1)$$

The constants, a_L and K_L, are the characteristics of the Langmuir equation, where K_L is the Langmuir equilibrium constant and the ratio a_L/K_L gives the theoretical monolayer sorption saturation capacity, X_m. These values are shown in Table 1, although it should be noted that some of the X_m values were not derived from an analysis of equation (1) but were simply read off the experimental equilibrium curve by interpolation.

The Freundlich expression is an empirical equation based on sorption onto a heterogeneous surface[81]. The Freundlich equation is represented as,

$$q_e = q_F C_e^b \qquad (2)$$

The Freundlich equation generates an exponential shaped theoretical equilibrium curve.

A further empirical isotherm has been developed[82,83] incorporating three parameters,

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \tag{3}$$

The exponent, β, lies between 0 and 1 and this equation has more mathematical flexibility for curve fitting purposes. When $\beta = 0$ equation (3) reduces to the Langmuir expression, equation (1), and when $\beta = 1$, equation (3) reduces to Henry's Law. Solving equation (3) for three unknown constants is obviously more complex than solving equation (1) and (2). However, by introducing a minimising function to compare the theoretical q_e values with the experimental q_e values a simple software program quickly produces the three values. There are several other isotherm equations available for analysing experimental sorption equilibrium data, including the Toth[84], the Dubinin-Radushkevich[85,86] and the BET[87] isotherms. However, these latter three approaches have mostly been applied to gas-solid systems. Table 1 shows that over fifty percent of the references do not perform an isotherm analysis on the experimental data. In the remaining cases, less than five percent use two or more isotherms in an attempt to characterize the best-fitting isotherm. In most cases, the Langmuir isotherm provides the best fitting isotherm model and has been used by most researchers applying only one model. From the limited data available, it appears that the sorption of copper onto most biosorbents is a homogeneous process with a constant energy of activation and that a monolayer saturation capacity is reached.

2.4 Kinetics of Copper Sorption

In order to investigate the mechanism of sorption and potential rate controlling steps such as mass transport and chemical reaction processes, kinetic models have been used to test experimental data. These kinetic models included the pseudo-first order equation, the pseudo-second order equation and the Elovich equation.

2.4.1. The Pseudo-First Order Equation

The pseudo-first order equation of Lagergren[88] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{4}$$

where q_e and q_t are the sorption capacities at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant of pseudo-first order sorption, (1/min). After integration and applying boundary conditions, t = 0 to t = t and $q_t = 0$ to $q_t = q_t$; the integrated form of equation (4) becomes :

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{5}$$

The equation applicable to experimental results generally differs from a true first order equation in two ways[89]:

a. the parameter $k_1(q_e - q_t)$ does not represent the number of available sites;

b. the parameter $\log(q_e)$ is an adjustable parameter which is often not found equal to the intercept of a plot of $\log(q_e - q_t)$ against t, whereas in a true first order sorption reaction $\log(q_e)$ should be equal to the intercept of a plot of $\log(q_e - q_t)$ against t.

In order to fit equation (5) to experimental data, the equilibrium sorption capacity, q_e, must be known. In many cases q_e is unknown and as chemisorption tends to become unmeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount[90]. In most cases in the literature, the pseudo-first order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 20 to 30 minutes of the sorption process. Furthermore, one has to find some means of extrapolating the experimental data to t = ∞, or treat q_e as an adjustable parameter to be determined by trial and error. For this reason, it is therefore necessary to use trial and error to obtain the equilibrium sorption capacity, q_e, in order to analyse the pseudo-first order model kinetics. In over 50% of literature references, based on analysing sorption kinetics, the authors did not measure an equilibrium isotherm.

2.4.2. The Pseudo-Second Order Equation

If the rate of sorption is a second order mechanism, the pseudo-second order chemisorption kinetic rate equation is expressed as:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{6}$$

where q_e and q_t are the sorption capacity at equilibrium and at time t, respectively (mg/g) and k is the rate constant of pseudo-second order sorption, (g/mgmin.) For the boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$; the integrated form of equation (6) becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \tag{7}$$

which is the integrated rate law for a pseudo-second order reaction. Equation (7) can be rearranged to obtain:

$$q_t = \frac{t}{\frac{1}{kq_e^2} + \frac{t}{q_e}} \tag{8}$$

which has a linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{9}$$

Equation (9) does not have the problem of assigning as effective q_e. If pseudo-second order kinetics are applicable, the plot of t/q_t against t of equation (9) should give a linear relationship, from which q_e and k can be determined from the slope and intercept of the plot and there is no need to know any parameter beforehand.

2.4.3. The Elovich Equation

The Elovich equation[91] is generally expressed as follows:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \qquad (10)$$

where q_t is the sorption capacity at time t (mg/g) and α is the initial sorption rate (mg/gmin) and β is the desorption constant (g/mg) during any one experiment.

To simplify the Elovich equation, Chien and Clayton[92] (1980) assumed $\alpha\beta t >> 1$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ equation (9) becomes[93,94]

$$q_t = \beta \ln(\alpha\beta) + \beta \ln(t) \qquad (11)$$

Thus, the constants can be obtained from the slope and the intercept of a straight line plot of q_t against ln(t). Equation (11) will be used to test the applicability of the Elovich equation to the kinetics of sorption.

The pseudo-second order equation is based on the sorption capacity on the solid phase. It deserves particular attention in the present discussion, because contrary to the other models it predicts the behavior over the whole range of studies and a pseudo-second order equation and is in agreement with a chemisorption mechanism being the rate controlling step.

Other data [34] from literature were also tested by plotting t/q_t against t for the sorption of copper (II) onto bottom ash according to equation (6). The agreement of experimental data and the pseudo-second order equation is much better than those for equations (4) and (11). The correlation coefficient for copper is 1.00.

A model[95] based on external mass transfer used an external mass transfer coefficient as the rate controlling coefficient to predict the concentration versus time decay curve for the sorption of copper onto peat and lignite[96]. The equation is :

$$\ln\left(\frac{C_t}{C_o}-\frac{1}{1+m_sK_L}\right)=\ln\left(\frac{m_sK_L}{1+m_sK_L}\right)-\left(\frac{1+m_sK_L}{m_sK_L}\right)k_fS_st \tag{12}$$

This correlation gives good agreement to support the film diffusion single-resistance assumption at low surface coverage but not at high surface coverage, indicating an additional rate controlling step might be involved such as intraparticle diffusion or that the sorption process may be reaction based.

The pseudo-first-order kinetic model has been used extensively to describe the sorption of metal ions onto sorbents. In the case of copper these have been designated in the kinetic model column of Table 1. The main disadvantages of this model are (i) that the linear equation (5) does not give theoretical q_e values which agree with experimental q_e values, and (ii) the plots are only linear over the first thirty minutes, approximately. Beyond this initial thirty minutes period the experimental and theoretical data do not correlate well. Various authors have made proposals for these deviations. One suggestion for the differences in the q_e values is that there is a time lag, possibly due to a boundary layer or external resistance controlling at the beginning of the sorption process[89,95]. This time lag is difficult to quantify and does little to help rationalise the differences in experimental and theoretical q_e values. In terms of the short time correlation between experimental and theoretical data for the Lagergren[88] pseudo-first order model, it has been proposed that another first order reaction[97-99] supersedes the first or another reaction of another order becomes predominant. No mechanisms have been proposed for this stage by any authors.

2.5 Mechanism of Copper Sorption onto Biosorbents

From the outset it is apparent that no single mechanism will describe the sorption of copper ions onto the wide array of biosorbents and minerals described in this paper. In the case of conventional synthetic ion exchangers the sorption capacity is dependent on the number of available H^+ or Na^+ ions for exchange. Ions are readily exchanged under suitable operating conditions and pH and the rate of exchange is almost instantaneous. In the case of the carbon systems reviewed in this study, the acid washed, activated powdered carbons have the high capacities due to the large external surface area, but more significantly the presence of H^+ ions in the surface layers capable of ion exchanging with copper. Most of the conventional cellulosic or pith based materials[33, 38, 51,55] have relatively low capacities due to the lack of ion exchange chemicals and the mechanism is probably largely physisorption. Work on coconut husk[53] indicated that treatment of the husk with acid dye increased the copper sorption capacity of the husk three fold. The ionic nature of acid dyes obviously enhanced the chemisorption capacity of the husk. A capacity of 56.7 mg copper/g sorbent has been reported[39] for chitosan. This material is a deacetylated polysaccharide extracted from the shell wastes of crustacea and has a large number of amine groups containing a lone pair of electrons available for chelation.

2.5.1. Sorption Mechanism of Chitosan

The chemical structures of chitin and chitosan are shown in Figure 1. The bipolymer of chitosan consists of D-glucosamine with β-(1,4) bonds that provide the focus for metal absorption in dilute metal ion solutions. The metallic ions normally absorb onto the amino and hydroxyl groups to form a metal complex with the polymer chains. However, chitosan is selective for metal ions, it only uptakes the transition and post-transition metals but does not absorb for the alkali and alkaline earth metals[100]. Although many papers have been published on the chitosan-metal sorption mechanism, mainly as a function of metal ion, coordination index, hydrolysis constants, precipitation mechanism, deposition of metal aggregate mechanism[101], ion-exchange properties and complexation, however, its metal adsorption mechanism has still not yet been fully explained. In contrast, the sorption efficiency for the soluble chitosan with a large number of metal ions and their chelating properties have been found to obey the Irving-Williams and Mellor-Maley series[102]. A simple chelation scheme for metal ions sorbing onto chitosan is shown in Figure 2 for the sorption of metal ions from ammonium nitrate solution.

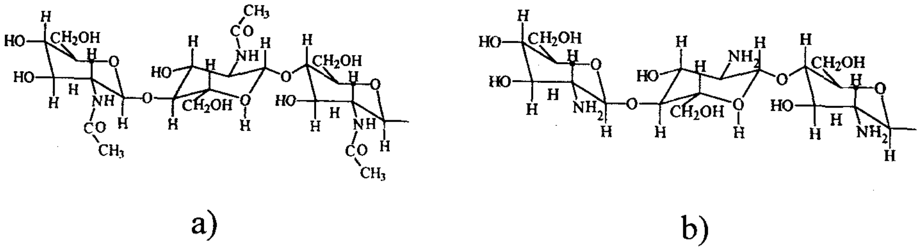

FIGURE 1

Molecular repeating units of a) chitin and b) chitosan.

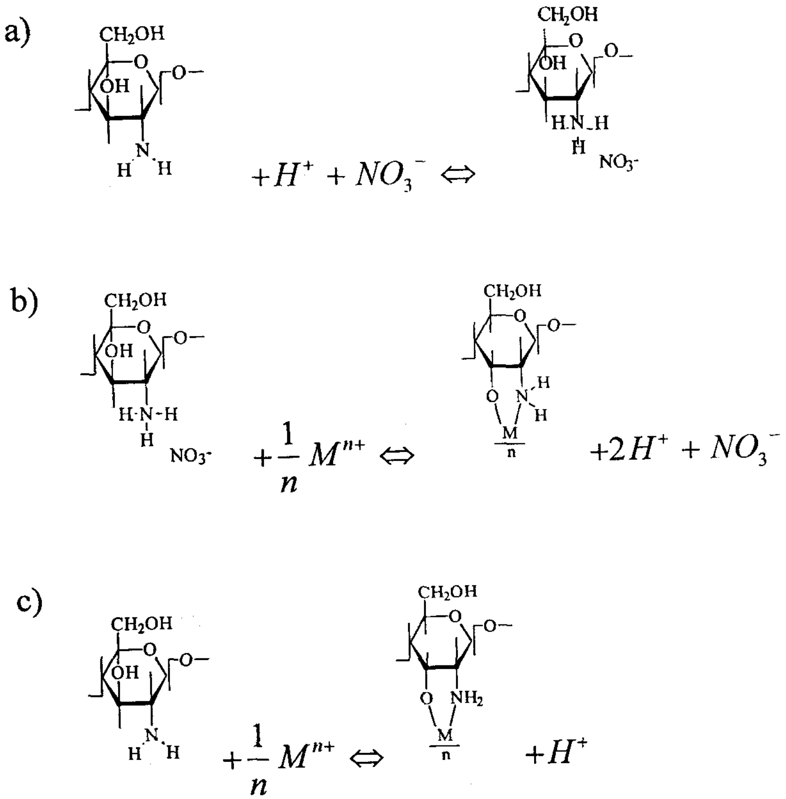

FIGURE 2

Adsorption of n-valent metal ion on chitosan[103] from ammonium nitrate solution through a) protonation, b) chelation and c) total reaction.

Inoue *et al*[104] reported the capacity of metal sorption becomes weaker when the chitosan polymers are dissolved in acidic media due to the crosslinking between the polymers. The copper sorption abilities and the uptake efficiencies can be increased by modifications to chitosan, such as grafting of specific funtional group - pyridine[105], preparation of chitosan-based adsorption gels[106] and crosslinked chitosan resin[107].

Spectroscopic studies revealed that there is a disagreement in the literature regarding the coordination modes for the chitosan-copper complex. A "bridge model" has been proposed[108] where the copper ion is coordinated with four nitrogen atoms of the intra- and inter-chitosan chains and secondly a "pendant model" which states that the copper ion is attached to an amino group of the chitosan chain, like a pendant[109]. However, it has been recently confirmed by the technique of electrospray mass spectrometry[104] that the Cu (II) is co-ordinated to the C(1)-alkoxide, the four amine nitrogens of chitosan tetrasaccharide and an anion. The solution equilibria for the chitosan tetrasaccharides[104] with Cu (II) are shown as follows :

$$M^- + H^+ \leftrightarrow MH \tag{13}$$

$$M^- + 2H^+ \leftrightarrow MH_2{}^+ \tag{14}$$

$$M^- + 3H^+ \leftrightarrow MH_3{}^{2+} \tag{15}$$

$$M^- + 4H^+ \leftrightarrow MH_4{}^{3+} \tag{16}$$

$$M^- + 5H^+ \leftrightarrow MH_5{}^{4+} \tag{17}$$

$$M^- + Cu^{2+} \leftrightarrow [MCu]^+ \tag{18}$$

$$M^- + 2Cu^{2+} \leftrightarrow [MCu_2]^{3+} \tag{19}$$

$$M^- + Cu^{2+} + OH^- \leftrightarrow [MCuOH] \tag{20}$$

$$M^- + 2Cu^{2+} + OH^- \leftrightarrow [MCu_2OH]^{2+} \tag{21}$$

$$M^- + 2Cu^{2+} + 3OH^- \leftrightarrow [MCu_2(OH)_3] \tag{22}$$

$$M^{-} + 2Cu^{2+} + 4OH^{-} \leftrightarrow [MCu_2(OH)_4]^{-} \qquad (23)$$

2.6 Diffusion and Sorption Models

Various models of adsorption isotherms have been discussed in the earlier section based on the Langmuir and Freundlich equations which quantitatively describe the equilibrium of a solute separated between the liquid and solid phases.

Sorption mass transport kinetics are mainly controlled by various steps including diffusion processes. They are i) metal transfer for the bulk solution to the boundary film bordering the sorbent surface; ii) metal transport from the boundary film to the surface of the sorbent; iii) transfer of the metal from the surface to the intraparticular active sites; iv) uptake of metal ion on the active sites, via complexation, sorption and intraparticular precipitation phenomena and; v) heat diffusion in the particle and iv) heat diffusion in the solution.

Mechanisms of diffusion of chitosan-copper sorption has been studied[39] as a single external diffusion process (film mass transfer control), intraparticular diffusion process (as solid or pore diffusion) or a combined phenomena[110,111].

2.7 Sorption Mechanism of Biomass

The mechanism of copper sorption onto biomass has been proposed by Ruhling and Tyler[112] to use the model of ion-exchange mechanism, the woodland moss had a high capacity to sorb the heavy metal ions from dilute solutions. Lee and Low[12] reported the maximum capacity of moss - *Calymperse delessertill Besch* in a dilute copper solution was 27.1 mg/g which was derived from the Langmuir isotherm. In general, cell tissues consist of exchangable forms (cationic/anionic) of active sites, the overall charge of the cell is based on the extent of its isoelectric point. As a result, a net negative charge must predominate to attract the metal cations.

Metal uptake mechanisms are associated with two basic steps. Initially, a rapid mechanism on the metal uptake on the cell wall surface binding which is known as extracellular binding and then the mechanism proceeds to a subsequent slow active uptake due to membrane transport of the metal ions into the cell - intracellular binding. These complex bindings are dependent on the metal ion and the biological system[113]. The adsorption capacity of copper for *Zoogeloea ramigera* is 171.5 mg/g and was reported by Norberg and Rydin[114] and Norberg and Persson[115]. Its copper uptake mechanism was demonstrated by adsorption onto extracellular polymer.

Furthermore, sorption process may proced by chelating, complexing, ion entrapping, chemical sorption and physical forces between the cell walls and the membranes. It depends on the origin of the biomass, the species of biomass used and the biological system[116]. The cell containing functional groups may have attract forces to bind the metal ions from dilution solutions, such as fungi have a polysaccharide structure, nucleic acids provide the amino and phosphate groups, proteins contain the amino, amido, sulfhydryl and carboxyl groups, hydroxyls in polysaccharides and mainly carboxyls and sulfates in the polysaccharides of marine algae. However, in certain cases in the presence of these functional groups, adsorption may not take place and this is probably due to the steric barriers, structural confirmations, strain and stress or other reasons.

Peanut hull carbon[65] and the modified coconut coir[64] have a similar ion-exchange process mechanism for the removal of the copper ion. In these cases, the pure carbon surface is considered to be a non-polar but contains some oxygen complexes hydrolyse water molecules C_xO, CO_x and C_xO_2 which are formed as shown :

$$C_xO + H_2O \rightarrow C_XOH_2^{2+} + 2OH^- \tag{24}$$

$$CO_x + H_2O \rightarrow C(OH)_x + xOH \tag{25}$$

$$C_xO_2 + H_2O \rightarrow C_xO^{2+} + 2OH^- \tag{26}$$

In the preparation of these carbons, they are initially treated with H_2SO_4, $NaHCO_3$ and $(NH_4)_2S_2O_8$. Hence, groups of C_xONa^+, $C_xONa_2^{2+}$, C_xSO_3Na and $C_xONH_4^+$ are also assumed to be present in the medium for the exchange with H$^+$. These mechanisms are described as shown:

$$C_xONa^+ + H^+ \rightarrow C_xOH^+ + Na^+ \tag{27}$$

$$C_xONa^+ + 2H^+ \rightarrow C_xOH_2^{2+} + Na^+ \tag{28}$$

$$C_xONa_2^{2+} + 2H^+ \rightarrow C_xOH_2^{2+} + 2Na^+ \tag{29}$$

$$C_xSO_3Na + H^+ \rightarrow C_xSO_3 + Na^+ \tag{30}$$

Adsorption of copper ions in solution releases some free H$^+$ as well as the Na$^+$ when the pH is decreased. The released reactions are as follows :

$$2C_xNa^+ + Cu^{2+} \rightarrow (C_xO)_2Cu^{2+} + 2Na^+ \tag{31}$$

$$C_xONa_2^{2+} + Cu^{2+} \rightarrow C_xOCu^{2+} + 2Na^+ \tag{32}$$

$$2C_xSO_3H + Cu^{2+} \rightarrow (C_xSO_3)_2Cu + 2H^+ \tag{33}$$

$$2C_xSO_3Na + Cu^{2+} \rightarrow (C_xSO_3)_2Cu + 2Na^+ \tag{34}$$

Sorbents should be considered in terms of their large surface areas and high porosities as well as the chemical and physical properties of the sorbent. However, peat and lignite are generally dark brown in colour, having a spongy consistency and are partially fossilised plant matter that is formed in wet areas under partially anaerobic conditions, where the rate of accumulation of plant matter is greater than that of decomposition as a result of incomplete decomposition of the plant. Peat is a complex material containing mainly organic residues such as lignin, chelating[117], and cork-like tissues which are the main constituents of plants. Other component substances include resins, waxes, proteins, dyes[118]. Chemical adsorption can occur by the polar functional groups of lignin, which include alcohols, aldehydes, ketones, acids phenolic hydroxides and ethers as chemical bonding agents[119]. Because of the fairly polar character of peat, the specific adsorption capacity for dissolved solids such as transition metals and polar organic molecules is very high. According to Asplund *et al*[120], peat has a extensive specific surface area (> 200 m^2/g) and is extremely porous (95%). Therefore, peat is a greatly polar and porous material. Poots and McKay[121] have also reported the specific surface area of a peat moss using dye solutions, p-nitrophenal and mercury porosimetry. The specific surface areas are not only dependent on the chemical nature of the solute and adsorbent but also the molecular dimensions of the solute. A value of 27 m^2/g was obtained for nitrogen, 11.8 m^2/g for acid dye, and 100 m^2/g for basic dye[121]. It shows the presence of negatively charged molecules associated with the polar functional groups of peat as well as the exchange adsorption occurring with hydrogen ions. The natural capacity of peat to retain cations is related to the pH of solution. At pH values above 8.5, peat itself is not stable. At low pH, below 3.0, most metals will be leached from peat. Between these pH values, it is known that peat can adsorb most metals in a fairly efficient way[3]. The peat particles are surface-active and have a high cation-exchange capacity[122] (90-150 meq/100 g dry matter). Szalay[123] and Trujillo *et al*[124] reported that a great number of cationic elements are sorbed, and that electrochemically equivalent quantities are sorbed from cations of different valencies by given peat preparations.

A number of tests on sorption of copper using peat have taken place and it has been shown that there are wide variations between the amounts of copper taken up by peats from differing sources and acid pretreated peats. In particular, all the peats presented in Table 1 with a sorption capacity greater than 25mg copper ions/g peat are acid washed peats. This strongly confirms the earlier proposed mechanism that peat acts as a hydrogen ion exchanger to remove copper from wastewaters. The physical and chemical properties of the peat are said to depend on a variety of factors, such as the nature of the plants from which it has originated, the properties of the water in which the plants were growing (in particular the oxygen status, the pH and the dissolved bases), and the moisture relations during and following its formation and accumulation[125].

In addition, to pH influencing the extent of copper biosorption, it is likely that the effects of characteristics of the water matrix also influence metal biosorption. Ravichandran *et al*[126] reported that dissolved organic matter is usually present along with metal ions in research on the enhanced dissolution of cinnabar, mercuric sulphide, by dissolved organic matter. This paper demonstrates the importance of the hydrophobic characteristics of dissolved organic matter, particularly humic and fulvic acids, in dissolving mercury ions from cinnabar ore. The interactions and complexation reactions between metal ions and dissolved organic matter has been the subject of a comprehensive review by Buffle[127]. The mechanisms proposed for the mercury-fulvic and mercury-humic acid systems included surface complexation of mercury and oxidation to surface sulphur species by the organic matter.

3. CONCLUSION

While peat is a good model system, and is certainly the most widely studied system, there are many other biosorbent materials available for metal sorption. For copper ions, one can compare biosorbents, such as tree bark, straw, peanut husks and peat moss, with other sorbents like activated carbon, crushed coal, inorganics like activated alumina, and especially fabricated ion exchangers. Comparisons show some of these materials, such as ion exchange resins and activated carbon, are effective but expensive; other sorbents like fly ash, clay and sawdust are inexpensive and poor sorbents; still some materials fail for other reasons, for instance activated alumina is effective in removing heavy metals, but is readily soluble under extreme pH conditions.

The mechanism and kinetics of copper ion sorption onto biosorbents depends on the chemical characteristics of the biosorbent material and on the experimental conditions particularly copper ion concentration and biosorbent mass. In the present paper, it has been shown that intra-particle diffusion, external mass transfer and chemical binding reactions can take part in the rate-controlling steps, the precise mechanisms of metal ion binding has not been established for many of the biosorbents. The range of materials used in sorption trials is, therefore, very considerable, extending from highly humified and polymerised lignocellulosics, like peat, through less lignified materials like coir, to substituted cellulosics, and biomass of one sort or another containing substantial amounts of amino material. Most of these materials have been investigated as sorbents only recently, compared with peat's long history. Since the sorptive processes in peat (the most comprehensively studied biosorbent) are not, by any means, understood fully, it is hardly surprising that there is still much to learn about these other biosorbents.

4. NOMENCLATURE

a	Langmuir isotherm constant (dm^3/mg)
a_R	Redlich-Peterson isotherm constant (dm^3/mg)
b	Feundlich isotherm exponent
C_e	equilibrium liquid-phase concentration (mg/dm^3)
C_o	initial liquid-phase concentration (mg/dm^3)
C_t	liquid-phase concentration at time t (mg/dm^3)
d_p	mean sorbent particle diameter (μm)
F	Freundlich isotherm equation
h	initial sorption rate at $t=0$ (mg/gmin)
k	pseudo-second-order sorption rate constant (g/mgmin)
k_1	pseudo-first-order sorption rate constant (1/min)
k_f	external mass transfer coefficient (cm/s)
k_i	intraparticle diffusion rate parameter ($mg/gmin^{0.5}$)
K_L	Langmuir isotherm constant, (dm^3/g)
K_o	temperature independent preexponential factor (g/mgmin)
K_R	Redlich-Peterson isotherm constant (dm^3/g)
L	Langmuir isotherm equation
m_s	mass of sorbent per unit volume of solution (g/dm^3)
q_e	amount of solute sorbed at equilibrium (mg/g)
q_F	Freundlich isotherm constant
q_t	amount of solute sorbed at time, t (mg/g)
r^2	linear regression analysis correlation coefficient (-)
R	universal gas constant (8.314 J/mol)
R_e	percentage solute removed from solution at equilibrium (%)

RP	Redlich-Peterson isotherm equation
t	contact time (min)
T	solution temperature (°C)
X_m	theoretical monolayer sorption saturation capacity (mg/g)

Greek letters

α	initial sorption capacity rate (mg/gmin)
β	desorption constant (g/mg)

Subscripts

e	equilibrium
f	film
s	solid

Superscripts

β	Redlich-Peterson isotherm exponent

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