REMOVAL OF COPPER AND CADMIUM IONS FROM DILUTED AQUEOUS SOLUTIONS BY LOW COST AND WASTE MATERIAL ADSORBENTS

MIHAELA ULMANU[1], ELENA MARAÑÓN[2*], YOLANDA FERNÁNDEZ[2], LEONOR CASTRILLÓN[2], ILDIKO ANGER[1] and DANIELA DUMITRIU[1]
[1] *Institute for Non-ferrous and Rare Metals, B-dul Biruintei 102, Bucharest, Romania;*
[2] *Department of Chemical Engineering and Environmental Technology, Higher School of Industrial Engineering, University of Oviedo, 33204 Gijón, Spain*
(author for correspondence, e-mail: emara@correo.uniovi.es, fax: 34(9) 8518 2382)*

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Abstract. The sorption of copper and cadmium ions using activated carbon, kaolin, bentonite, diatomite and waste materials such as compost, cellulose pulp waste and anaerobic sludge as sorbents is reported. Equilibrium isotherms were obtained for the adsorption of these metals in single and binary solutions. Bentonite presented the highest adsorption capacities for both copper and cadmium. A competitive uptake was observed when both metals are present; copper being preferentially adsorbed by all materials with the exception of anaerobic sludge. Equilibrium data were fitted to Langmuir and Freundlich models, with satisfactory results for most of the adsorbent-metal systems studied. Of all the adsorbents studied, bentonite and compost presented the highest removal efficiencies, reaching 99% for copper when cadmium is also present, for initial solution concentrations of up to 100 mg L^{-1}. Anaerobic sludge has a greater preference for cadmium, even in the presence of copper, with removal efficiencies of 98% for similar concentrations to those mentioned above.

Keywords: Author, please supply

1. Introduction

The presence of heavy metals in the environment is a major concern due to their toxicity. Many industrial processes produce aqueous effluents containing heavy metal contaminants. According to the World Health Organization, the metals of most immediate concern are aluminium, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead. In particular, cadmium and cadmium compounds are especially dangerous and highly toxic. The concentrations of these pollutants must be reduced by means of treatment to meet legislative standards. Concretely, the maximum permitted monthly average concentration in discharges for cadmium is 0.2 mg L^{-1} (Council Directive 83/513/CEE of 26 September, 1983).

Consequently, improved and innovative methods of wastewater treatment are continuously being developed to deal with removal of these components; fundamentally, methods that are economically feasible.

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In this present study, copper and cadmium were the chosen metals, due to their solubility over a wide range of pH and their presence in several industrial wastewaters. Cadmium, for instance, is a heavy metal that is found associated with zinc, lead and copper minerals and is emitted when these metals are processed. At the same time, it is produced in different industrial activities such as galvanising, pigments, stabilizers, thermoplastics, batteries and alloys. Copper is found in diverse industrial activities such as the electrical industry, alloys, algaecides, chemical catalysis and metal surface finishing.

Precipitation processes are the most widely used techniques for treating wastewater with high metal concentrations. The disadvantages of these processes are the large volumes of sludge containing heavy metals and the fact that the heavy metal content in the resulting effluents is still high. Thus, additional treatment such as ion exchange, reverse osmosis, or adsorption processes is required subsequent to the precipitation process in order to purify the effluent prior to discharge.

These latter processes may also be the primary metal-removal processes for wastewater with a low concentration of metals. However, some of them may incur high costs, which often cannot be taken on by small industries. Considerable interest has therefore arisen in the use of low-cost adsorbent materials for the elimination of these heavy metals when they are present in not very high concentrations.

Many materials found in nature present adsorption and ion exchange properties. The majority of these natural ion-exchange materials are made up of crystalline aluminosilicates with cation exchange properties, although certain aluminosilicates may also act as anion exchangers. As examples, we have zeolites, apatite, bentonite or diatomite. Many of these have been used to eliminate heavy metals from wastewater (Mellah and Chegrouche, 1997; Ulmanu *et al*., 1996).

Waste products have also been employed as adsorbents in the elimination of heavy metals, such as waste from bauxite refining (red mud) and fly ash (Apac *et al*., 1998) and blast furnace slag (Dimitrova, 1996). This last material was found to be an effective sorbent for Cu, Zn and Ni ions in a wide range of ion concentrations and pH values.

Activated carbon is a widely used adsorbent (Wasay *et al*., 1999), mainly due to its porous surface structure, which provides it with a high surface area. However, the high cost of activated carbon has led to the development of new materials with similar characteristics but lower costs. An example of these is peat, the adsorption capacity of which with respect to adsorbing metals has been reported in various studies (Chen *et al*., 1990; Gosset *et al*., 1986; Sharma and Foster, 1995).

In recent years, research has been carried out into the use of agricultural and forestry products for removing heavy metals from wastewater. Sawdust, for example, which is basically made up of lignine and cellulose, has been used in the removal of metals, such as Cu^{2+}, Hg^{2+}, Cr^{6+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+} and Mg^{2+} (Ajmal *et al*., 1998; Ulmanu *et al*., 1996). Other substances employed are: apple waste, coffee grounds, tea, walnut shells, walnut bark, peanut shells, rice husks, coconut husks, seeds, cotton, waste from the production of olive oil (Orhan and Büyükgüngör, 1993; Marañón and Sastre, 1991; Said *et al.*, 1992; Gharaibeh *et al.*, 1998). The bark from different trees also presents adsorbent properties with respect to heavy metals, as can be seen in the literature (Vázquez *et al.*, 1994).

The adsorbent properties of biological sludge for the removal of heavy metals have also been studied (Artola *et al.*, 1997; Gould and Genetelli, 1984). According to the results obtained (Artola *et al.*, 1997), the adsorption of metal by the sludge is a consequence of the interaction between the metals in the aqueous phase and the cell wall of the bacteria.

The main objective of this study was to investigate the adsorption of two heavy metals, copper and cadmium, onto different adsorbents materials such as activated carbon, low cost materials sorbents (diatomite, bentonite, kaolin) and waste materials (compost, cellulose pulp waste, anaerobic sludge) in single and binary solutions.

2. Materials and Methods

2.1. Samples

Sample solutions were prepared by dissolving the corresponding 'analytical grade' copper and cadmium soluble salts in double-distilled deionised water.

The concentrations used in the experiments varied between 65 and 200 mg L^{-1} for both metals. In the experiments carried out with binary solutions, equal concentrations of copper and cadmium were used.

2.2. Adsorbents

Seven adsorbent materials were studied: activated carbon, kaolin, bentonite, diatomite, compost, anaerobic sludge and cellulose pulp waste.

Activated carbon and kaolin were Merck quality materials. Bentonite and diatomite were from Romania; the main component of the diatomite was illite and the bentonite contained over 80% montmorillonite.

Compost was obtained from mowed garden grass, after it had undergone a natural composting process. The anaerobic sludge came from an anaerobic reactor used in research studies into the treatment of cattle waste (manure) (Castrillón *et al.*, 1998). Cellulose pulp waste, from the manufacture of paper paste, presented a cellulose content of 90%, and was supplied by the firm ENCE, located in Navia, Asturias, Spain.

The surface area was measured in all the materials by the BET method. Due to their residual character, other parameters, such as pH, inorganic matter and metals were also determined in the case of compost, anaerobic sludge and cellulose pulp waste. The results obtained are shown in Tables I and II.

TABLE I
Specific surface area of the adsorbents

Material	Specific surface area (m^2 g^{-1})
Active carbon	657.83
Kaolin	19.66
Bentonite	63.52
Diatomite	20.48
Compost	1.39
Anaerobic sludge	3.28
Cellulosic pulp waste	2.64

TABLE II
Characteristics of the waste material adsorbents

	Compost	Cellulose pulp waste	Anaerobic sludge
pH	7.3	9.0	8.0
Inorganic matter (% weight, db)	67.9	12.5	48.5
Metals (μg g^{-1}):			
Cd	1.05	0.79	2.55
Cu	29.90	19.50	62.31
Cr	2.41	2.59	20.00
Ni	8.69	8.17	16.86
Pb	20.00	6.20	20.33
Fe	6427.00	1189.00	3635.00
Zn	115.00	26.40	350.00

2.3. Procedures

Activated carbon, kaolin, bentonite and diatomite were used without any pre-treatment.

Compost was oven dried at 105 °C for 24 hr, after which it was manually ground in a mortar and then screened to eliminate the coarser sizes and so as to employ a homogeneous particle size in all the assays, ranging between 0.43 and 1.0 mm. This was carried out using a Retsch screening apparatus.

The anaerobic sludge, on being taken out of the reactor, was dried in a Velp Scientific frigothermostat model foc 225d at a temperature of 35 °C for several days. Once dry, it was also manually ground and then screened to obtain a particle size ranging between 0.43 and 1.0 mm.

The cellulose pulp waste was used without any further treatment other than oven drying at 105 °C. It was neither ground nor screened, due to its fibrous structure.

The determination by means of the BET method of the surface area of the different adsorbents was carried out in a Micromeritics Asap 2000 apparatus.

The adsorption studies were conducted in batch experiments at 22 °C using Erlenmeyer flasks, maintaining 2 g of adsorbent in contact with a 100 mL solution containing one or two metals for a period of 3 hr; previously determined as the optimal time for the adsorbents analysed (Ulmanu *et al.*, 1995). The pH of the solutions was kept under 6, adding NaOH or H_2SO_4 when needed; no precipitation of hydroxides being observed. After the 3 hr contact period, the solid was separated from the solution by filtration through 0.45 μm pore size filters and the concentration of metal ions in the solution was determined by atomic absorption using a Perkin Elmer Mod. 3110 atomic adsorption spectrophotometer.

Additionally, isotherm constants, necessary in the mathematical modelling of sorption systems, were obtained from representation of the equilibrium data as isotherm plots.

3. Results and Discussion

The adsorption isotherms obtained with single and binary solutions and the different adsorbent materials are shown in Figures 1 and 2. The best results are obtained with bentonite, since its metal uptake capacities are the highest and hence the residual metal concentrations in the solutions are the lowest. It can be observed that adsorption onto this material is practically linear in solutions containing one metal, whereas when both metals are present, linearity can only be observed for the lower concentrations (up to 90 ppm for Cd and 100 ppm for Cu). This may be due to the saturation of bentonite at higher concentrations, as can be observed in Figure 1.

For activated carbon, kaolin and diatomite, the presence of copper in the solution adversely affects the adsorption of Cd; on increasing the initial concentration of both metals, the adsorption capacity of the different materials for this latter metal decreases. This indicates that these materials have a greater selectivity for copper, in accordance with the experimental results found in the literature for similar materials, in which this behaviour is justified on the basis of the ionic size of the hydrated metal ion (Atanassova, 1999) or the different electronegativities of the two ions (Allen, 1995).

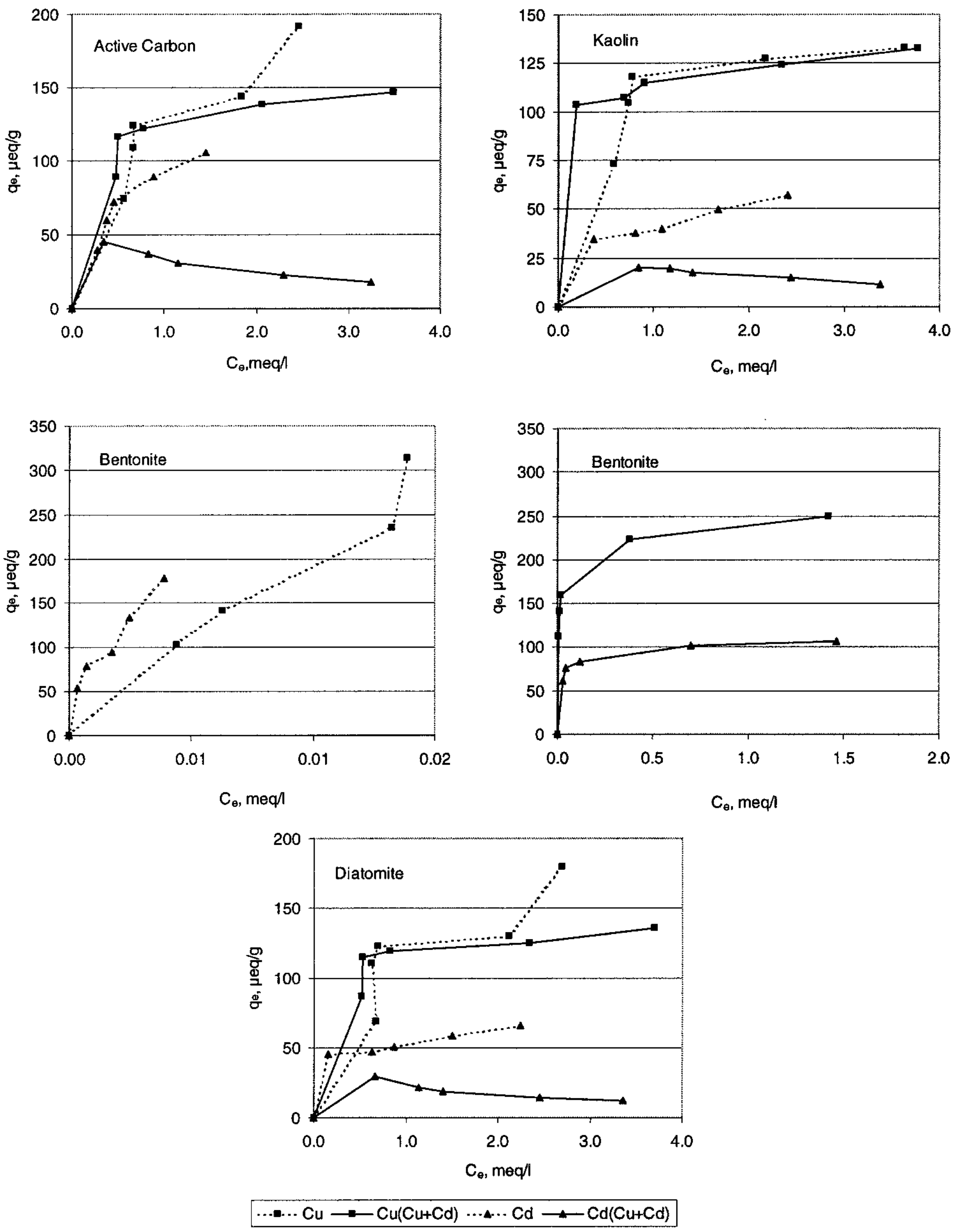

Figure 1. Experimental isotherms for the adsorption of Cu and Cd in single and binary solutions onto natural adsorbents.

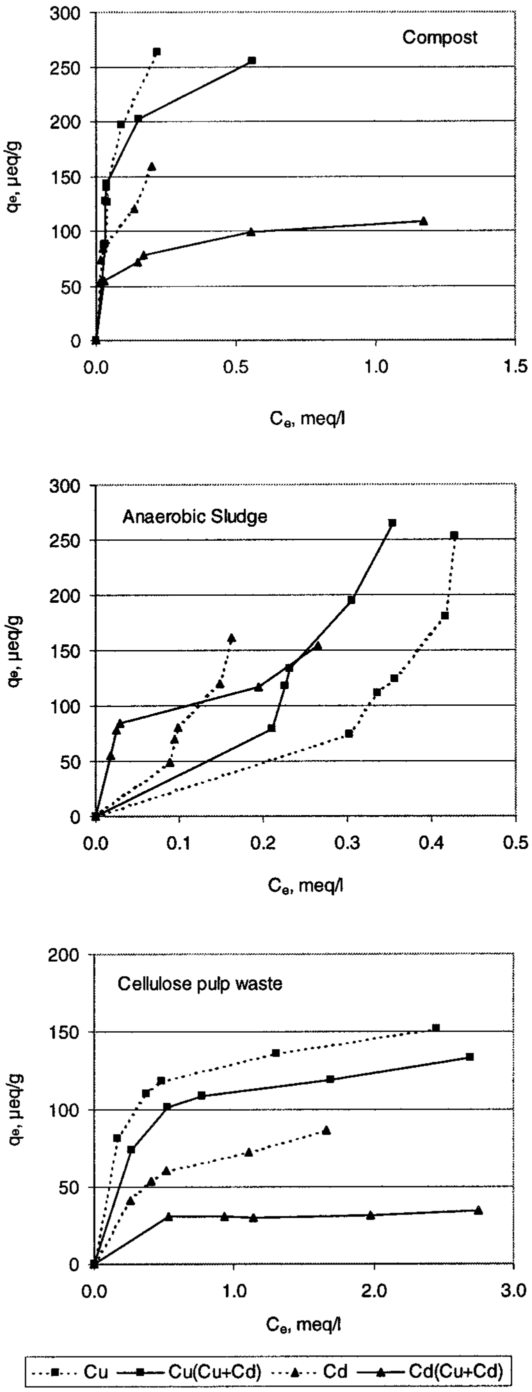

Figure 2. Experimental isotherms for the adsorption of Cu and Cd in single and binary solutions onto waste material adsorbents.

In the case of the waste materials (Figure 2), the anaerobic sludge behaves differently to the others, since the isotherms obtained are generally unfavourable, as can be seen by their concave form.

With respect to compost and cellulose pulp waste, it was found in both cases that the presence of one of the metals in solution decreases the uptake of the other and that this decrease is more pronounced for cadmium, indicating the greater affinity of these materials for copper.

The equilibrium data obtained in the different adsorbent-metal systems fitted the Langmuir and Freundlich models. The Langmuir isotherm fits the following equation:

$$q_e = \frac{Qkc_e}{1 + kc_e}$$

where

q_e	=	the specie concentration in the adsorbent;
k	=	the constant of Langmuir's equation, related to the enthalpy of the process;
Q	=	the adsorption capacity to form the single layer;
c_e	=	the concentration in the solution.

This isotherm is an example of a favourable isotherm and is applicable under the following hypothesis: a uniform surface of the solid, the absence of interaction between the different adsorbed molecules and adsorption in a single layer.

Freundlich's isotherm fits the following equation:

$$q_e = K_F c_e^{1/n}$$

where

q_e	=	the amount adsorbed per specified amount of adsorbent (mg g^{-1});
K_F	=	a constant related to the adsorption capacity;
c_e	=	the concentration in solution;
n	=	an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. For values in the range $0.1 < 1/n < 1$, adsorption is favourable (Namasivayam and Yamuna, 1992; Raji and Anirudhan, 1998).

This model is valid for heterogeneous surfaces and predicts an increase in the concentration of the ionic specie adsorbed onto the surface of the solid when increasing the concentration of said specie in the liquid phase.

Fittings were carried out separately for the single and binary systems. The results are shown in Figures 3 to 6 and in Tables III and IV. With regards to the single

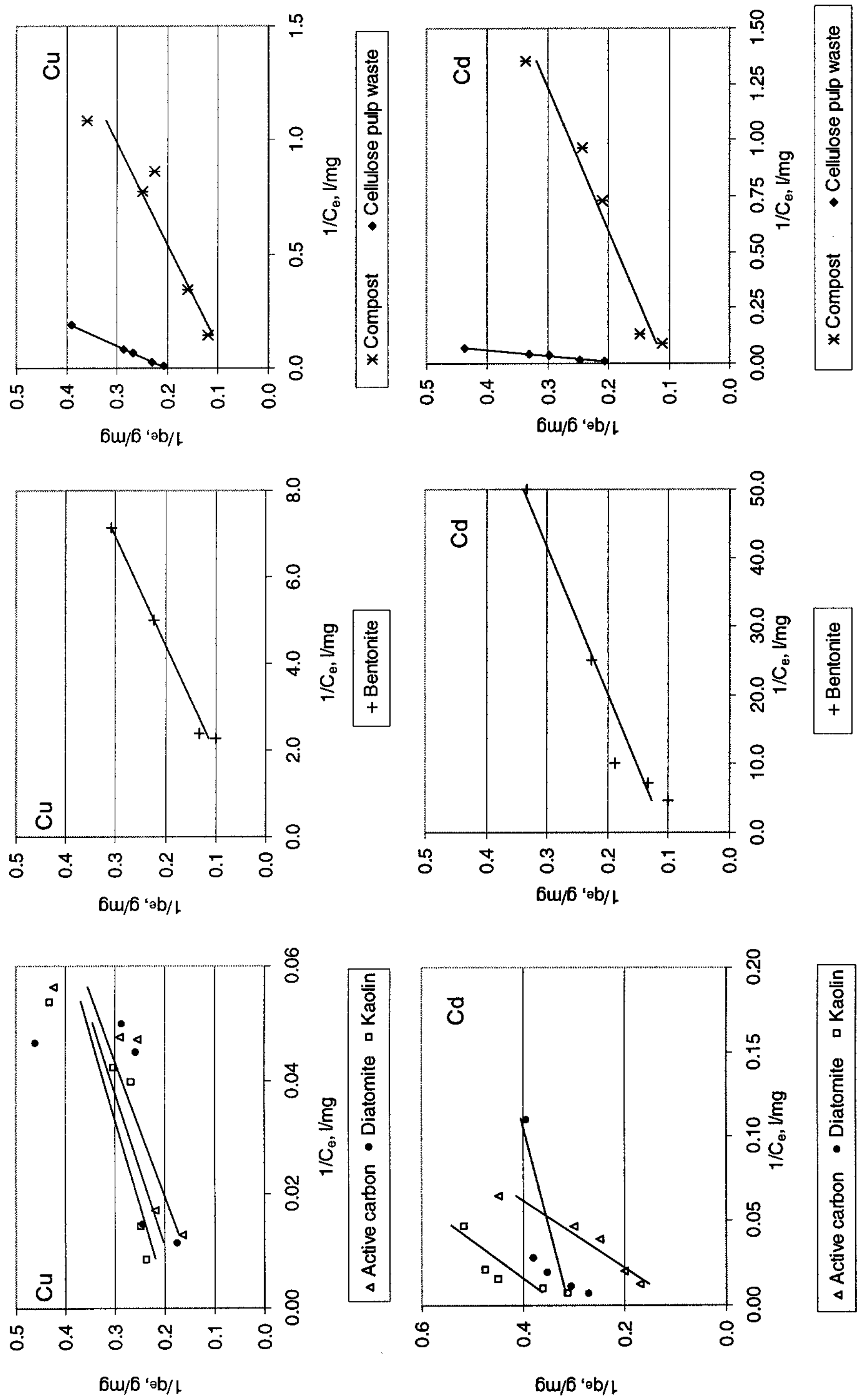

Figure 3. Langmuir isotherms for the adsorption of Cu and Cd in single solutions onto natural and waste material adsorbents.

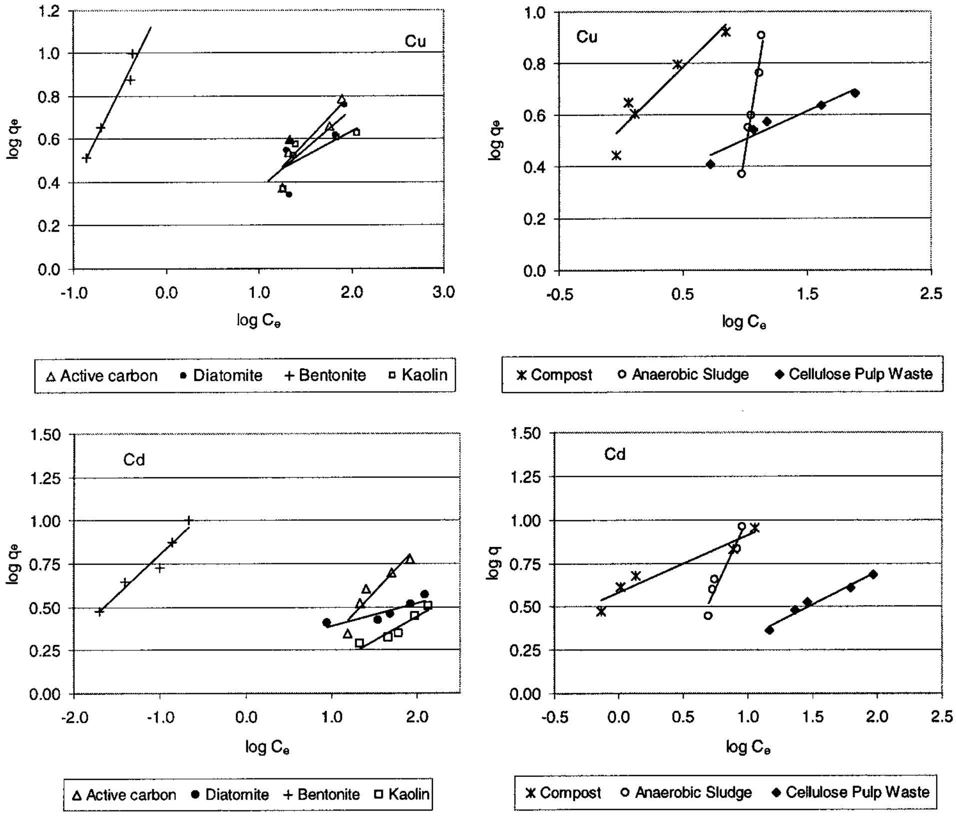

Figure 4. Freundlich isotherms for the adsorption of Cu and Cd in single solutions onto natural and waste material adsorbents.

systems, it can be seen that the Langmuir model fits the results better, in spite of the heterogeneity of many of the materials employed as adsorbents. The sole exception was obtained with the anaerobic sludge, for which it was not possible to carry out said fitting due to the fact that the adsorption of both metals onto this material produces unfavourable isotherms. In these solutions, the best fittings obtained with both models were for bentonite and the cellulose pulp waste, though the correlation coefficients are somewhat higher in the Langmuir model. With regards the adsorption capacity obtained for this model, considering the highest correlation coefficients, values of 12.77 mg g^{-1} were obtained for the Cu-compost system as opposed to 4.98 mg g^{-1} for the adsorption of Cu onto cellulose pulp waste. With respect to the adsorption of cadmium, the capacities obtained varied between 11.27 mg g^{-1} for the Cd-activated carbon system and 5.82 mg g^{-1} for Cd-cellulose pulp waste (Table III).

Adsorption onto anaerobic sludge fits the Freundlich model well, with values of $1/n > 1$, both for the adsorption of Cu as well as Cd, which correspond to unfa-

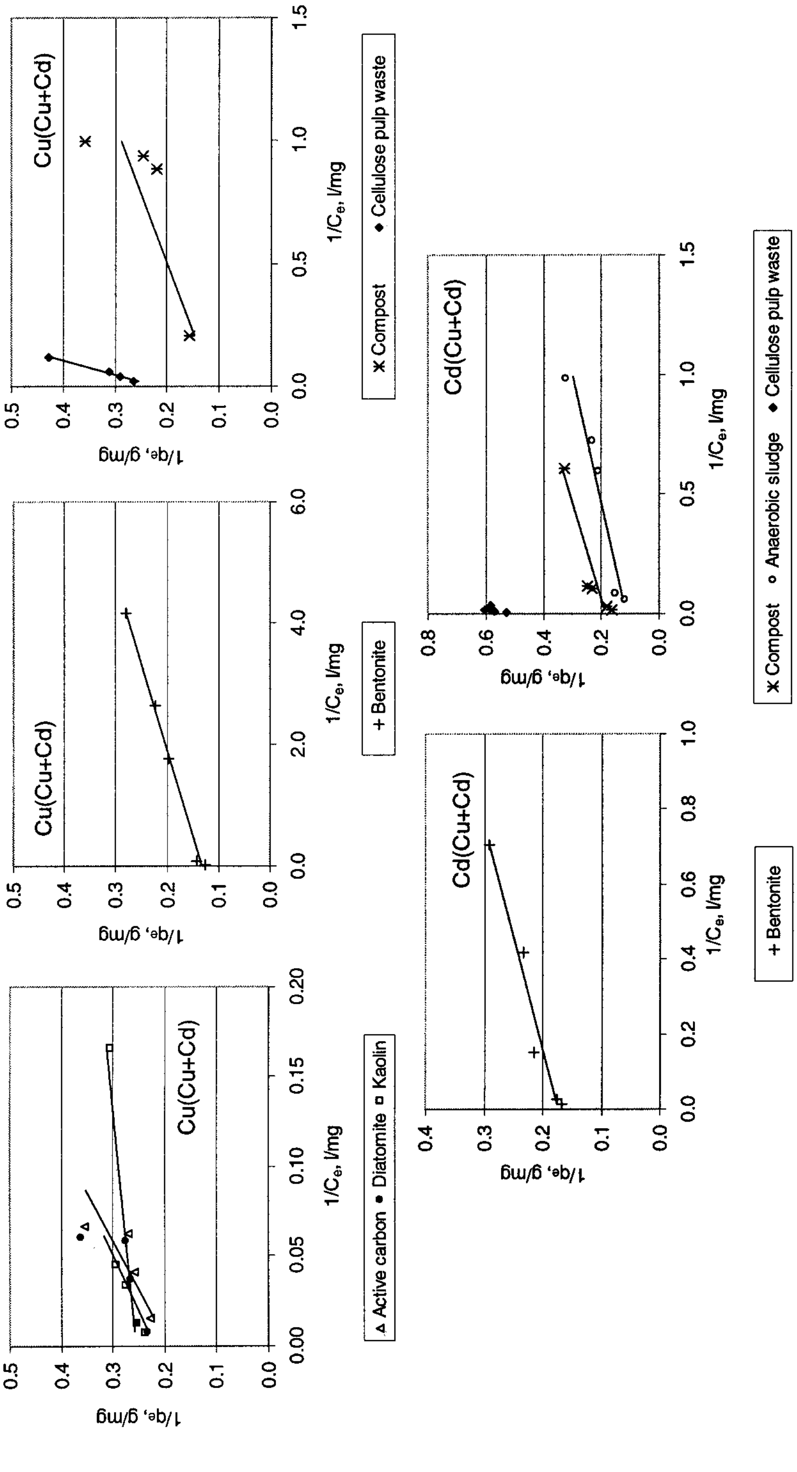

Figure 5. Langmuir isotherms for the adsorption of Cu and Cd in binary solutions onto natural and waste material adsorbents.

TABLE III

Langmuir and freundlich parameters for the adsorption of Cu and Cd in single solutions

Adsorbents	Langmuir constants						Freundlich constants					
	Copper			Cadmium			Copper			Cadmium		
	Q (mg g^{-1})	k (L mg^{-1})	r	Q^{a} (mg g^{-1})	k (L mg^{-1})	r	K_F	$1/n$	r	K_F	$1/n$	r
Active carbon	6.61	0.06	0.90	11.27	0.02	0.96	0.81	0.45	0.88	0.61	0.53	0.94
Kaolin	4.47	0.15	0.90	3.04	0.07	0.85	1.46	0.24	0.77	0.78	0.28	0.94
Bentonite	7.59	3.78	0.99	9.27	22.70	0.97	18.16	0.88	0.98	1.86	0.47	0.98
Diatomite	5.54	0.09	0.83	3.24	0.36	0.72	1.00	0.37	0.74	1.78	0.14	0.89
Compost	12.77	0.35	0.94	9.34	0.68	0.98	3.51	0.48	0.95	3.79	0.33	0.96
Anaerobic sludge	–	–	–	–	–	–	0.002	3.16	0.98	0.25	1.59	0.96
Cellulose pulp waste	4.98	0.20	0.99	5.82	0.05	0.99	1.92	0.22	0.97	0.90	0.37	0.98

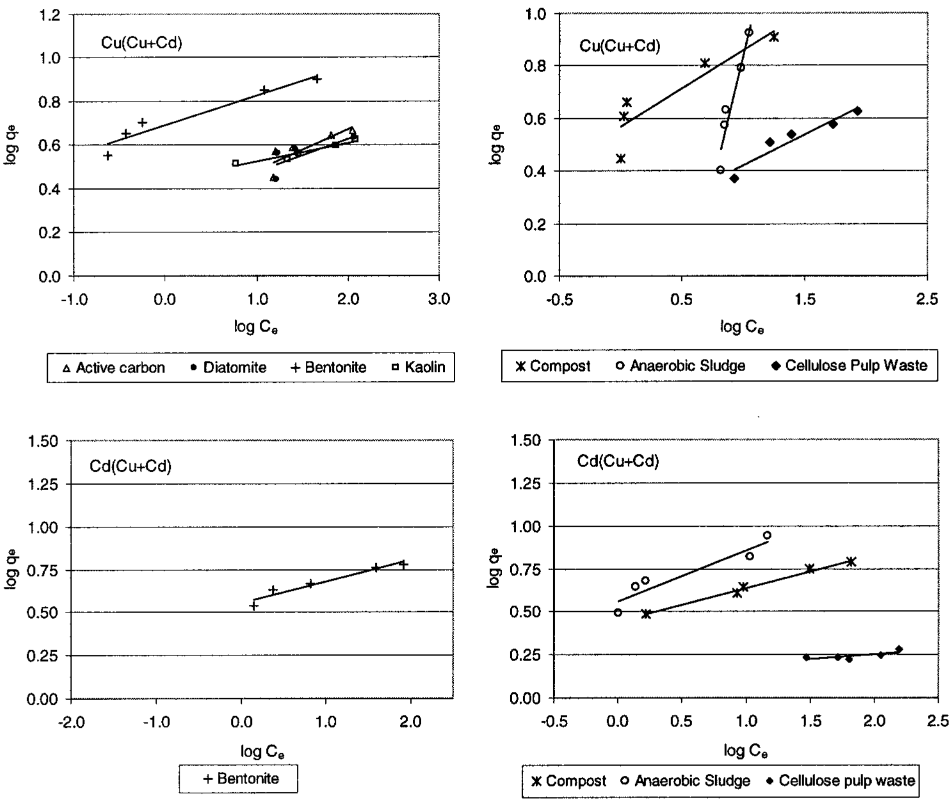

Figure 6. Freundlich isotherms for the adsorption of Cu and Cd in binary solutions onto natural and waste material adsorbents.

vourable adsorption equilibria, as can be appreciated in the shape of the isotherms (Figure 2).

Worth noting with regards to adsorption in binary systems is the fact that in the systems of Cd-activated carbon, Cd-kaolin and Cd-diatomite, the equilibrium data obtained does not fit the Langmuir and Freundlich models, although this fitting was possible in single systems. This may be because on increasing the amount of Cd in the solution, the expected increase in adsorption capacity is not produced but rather a decrease is produced (Figure 1), since as the amount of copper also increases, a competitive phenomenon arises between both species, copper being preferentially adsorbed.

The adsorption capacities obtained with the Langmuir model, considering the highest correlation coefficients, varied between 7.56 mg g^{-1} obtained for the Cu(Cu+Cd)-bentonite system and 4.36 mg g^{-1} for Cu(Cu+Cd)-kaolin. In the case of the adsorption of cadmium, and in the cases where the fitting was possible, the capacities varied between 8.94 mg g^{-1} for the Cd(Cu+Cd)-anaerobic sludge system and 5.36 mg g^{-1} for the Cd(Cu+Cd)-compost system (Table IV).

TABLE IV

Langmuir and freundlich parameters for the adsorption of Cu and Cd in binary solutions

Adsorbents	Langmuir constants						Freundlich constants					
	Copper (Cu+Cd)			Cadmium (Cu+Cd)			Copper (Cu+Cd)			Cadmium (Cu+Cd)		
	Q (mg g^{-1})	k (L mg^{-1})	r	Q^{a} (mg g^{-1})	k (L mg^{-1})	r	K_F	$1/n$	r	K_F	$1/n$	r
Active carbon	4.77	0.20	0.98	–	–	–	1.99	0.19	0.99	–	–	–
Kaolin	4.36	0.17	0.99	–	–	–	2.74	0.09	0.96	–	–	–
Bentonite	7.56	3.73	0.99	5.80	1.04	0.98	4.92	0.14	0.96	3.57	0.13	0.97
Diatomite	4.27	0.33	0.91	–	–	–	2.16	0.15	0.77	–	–	–
Compost	8.90	0.64	0.87	5.36	0.76	0.93	3.70	0.29	0.90	2.76	0.19	0.99
Anaerobic sludge	–	–	–	8.94	0.59	0.96	0.07	2.00	0.96	3.64	0.30	0.94
Cellulose pulp waste	4.55	0.13	0.99	1.82	0.39	0.72	1.55	0.23	0.95	1.38	0.06	0.71

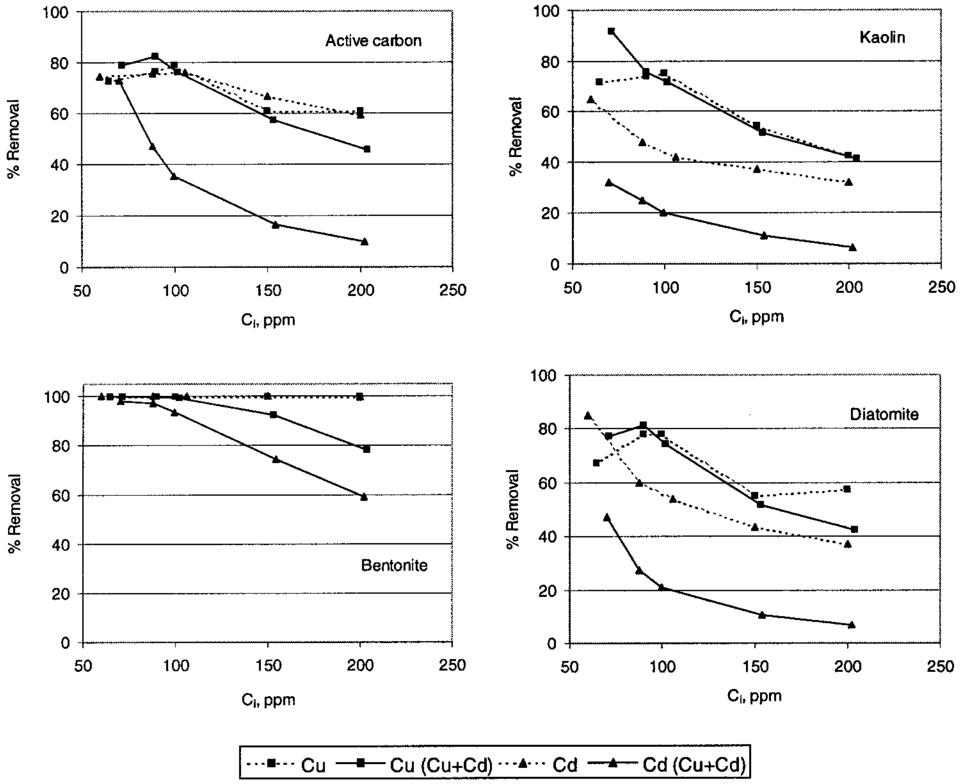

Figure 7. Removal efficiencies of the natural adsorbents for Cu and Cd in single and binary solutions.

Finally, it was determined how the removal capacity of both metals varied with the initial concentration and the presence of the other metal in the solution. The results are given in Figures 7 and 8, where it can be seen that the adsorbents that achieve the highest metal removal capacities are bentonite, followed by compost and anaerobic sludge. What is more, it can be seen that this removal capacity decreases as the initial concentration of the solution increases, as is to be expected. This behaviour becomes more pronounced when working with binary solutions, due to competition between the two metals for linking sites on the adsorbent material, this decrease being more pronounced in the case of cadmium.

4. Conclusions

Of the materials studied, bentonite, compost and anaerobic sludge exhibited the highest adsorption capacities, the lowest residual concentrations and thus the greatest removal capacities of copper and cadmium.

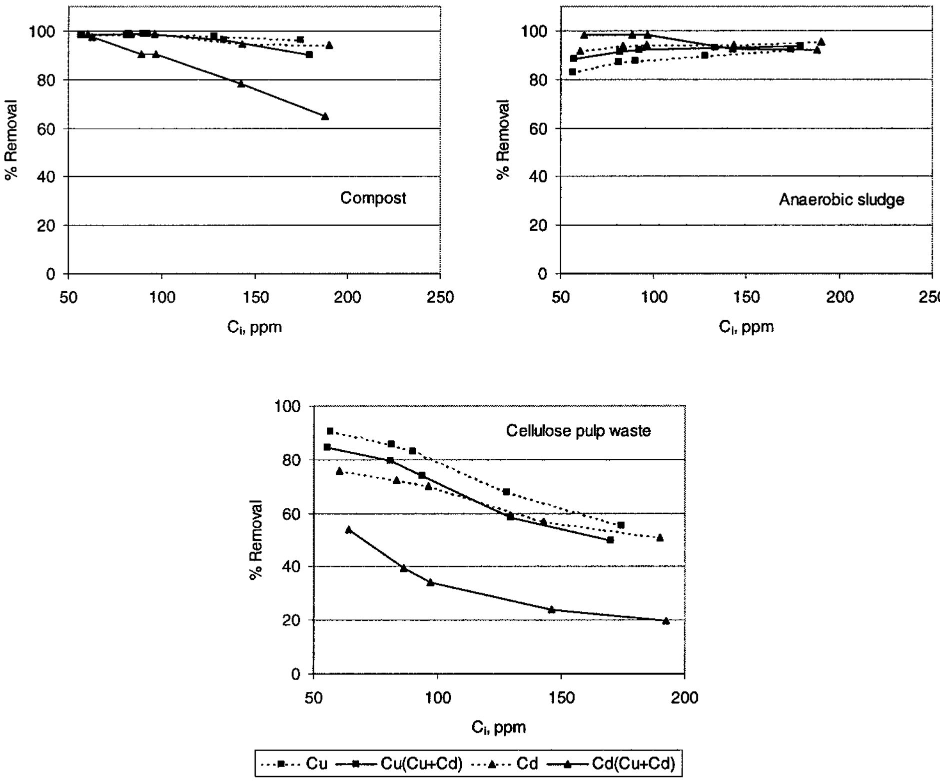

Figure 8. Removal efficiencies of the waste material adsorbents for Cu and Cd in single and binary solutions.

The presence of the two metals in solution creates competition for the linking sites on the adsorbent material. With the exception of anaerobic sludge, all the materials studied exhibited greater selectivity for copper.

In general, both the Langmuir and the Freundlich models achieve good fittings in single solutions. In the case of the sludge, it was not possible to apply Langmuir's model due to the unfavourable character of the isotherms obtained.

In binary systems, it was observed that within the range of concentrations studied, the presence of copper in the solution provoked a decrease in the adsorption capacity for cadmium of activated carbon, kaolin and diatomite. In these cases, it was not possible to carry out the fitting with said models.

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