A Multi-stage Batch Sorption Design with Experimental Data

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ABSTRACT: The sorption of lead ions on to peat in an agitated batch adsorber has been studied. A model has been developed for the design of a two-stage batch adsorber based on pseudo second-order sorption kinetics. The model has been optimised with respect to contact time in order to minimise total contact time to achieve a fixed percentage of metal ion removal.

INTRODUCTION

The ability of peat to remove metal ions has been well established (Coupal and Lalancette 1976; Viraraghavan 1993; Ho *et al.* 1995). Considerable information is available on the saturation capacities of peat for several metal ions based on equilibrium studies (Gosset *et al.* 1986; Allen *et al.* 1988; Viraraghavan and Dronamraju 1993) and several kinetic analyses have been presented to establish mass transfer and kinetic parameters (McKay and Allen 1983; Allen *et al.* 1989). However, the development of design models to predict the performance of metal ion sorption removal systems has received only limited attention with respect to batch or fixed-bed column sorber design (Volesky and Prasetyo 1994; Chen *et al.* 1995; Reed *et al.* 1996).

The lack of fixed-bed experimental data for metal ion removal systems has limited the application of classical simplified design models such as the BDST model (Tan *et al.* 1996) to metal ion sorption. Nevertheless, extensive metal ion sorption data are available for batch adsorber design. One classical simplified model (Lerch and Rathowsky 1967; McKay *et al.* 1980) has been applied extensively to dye removal from effluents (McKay 1982) and to the removal of organics from aqueous solutions (Aga *et al.* 1983). The model by McKay *et al.* (1980) is based on minimising the amount of sorbent used in a two-stage or n-stage batch contact system assuming sufficient residence time is allowed for the adsorption system to reach equilibrium. This model is suitable for expensive sorbents such as active carbon, zeolites, resins, sieves, etc. but optimisation, based on minimising the amount of adsorbent, is not necessarily always the main criterion in effective adsorber design. In congested industrial sites, the ability to process significant volumes of effluent to meet a fixed environmental emission limit in the minimum processing time is often of paramount importance. Due to size and space limitations on a manufacturing site, the capacity of a batch sorption plant may be limited. The ability of a batch sorption plant must then be designed based on the ability of this treatment system to process several batches of effluent per day; rather than using a minimum quantity of adsorbent and utilising a maximum contact time to achieve equilibrium saturation. This cannot be done in isolation of sorbent cost, but in recent years many relatively cheap sorbents have been identified such as peat (Coupal and Lalancette 1976), wood (Poots *et al.* 1976), pinus pinaster bark (Vázquez *et al.* 1994), waste rubber (Rowley *et al.* 1984), fly ash (Nonavinakere

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and Reed 1996), rice hulls (Suemitsu *et al.* 1986), bagasse pith (McKay *et al.* 1987), banana pith (Low *et al.* 1995) and tea leaves (Tan and Abd. Rahman 1988). These materials are ideal for contact time minimisation applications.

This paper describes studies of the sorption of lead ions on to peat and develops a two-stage batch adsorber design model. The model enables the contact time to be minimised to achieve a fixed percentage of metal ion removal using a fixed mass of sorbent material.

MATERIALS AND METHODS

The experiments were conducted with peat obtained from Klasmann-Deilmann GmbH, Germany. The peat, as supplied, was dried at a temperature of $90 \pm 2°C$ for 24 h and then screened to obtain a particle size range 500–710 µm peat. The peat was a sphagnum moss peat and elemental analysis gave the following composition: 48.8% C, 6.4% H, 42.9% O, 1.3% N and 0.6% S. The BET surface area was determined as 28.2 m^2/g and the absolute density of the peat as measured in paraffin oil was found to be 1250 kg/m^3.

The lead nitrate used in the experiments was supplied by Aldrich Chemicals (Catalogue No. 20358-0) with a purity of 99.99%. Stock solutions of lead nitrate [analytical grade $Pb(NO_3)_2$] were prepared in distilled water at concentrations of 3.26 g/dm^3. All solutions used in the study were diluted with distilled water as required. Lead(II) concentrations ranging from 100 mg/dm^3 to 500 mg/dm^3 were employed and agitation was carried out for 4 h until equilibrium was attained. Constant agitation was achieved using a six-bladed Perspex impeller and a shaft driven by a Heidolph (Germany) variable speed motor. The sorber vessel was constructed from PTFE and the baffles were made of Perspex. All parts were joined together using a special adhesive which was insoluble in water. The relative dimensions of the sorber vessel as shown in Figure 1 are presented in Table 1. All contact investigations were carried out using a baffled agitated 2 dm^3 sorber vessel and a constant agitation speed of 400 rpm. The vessel contained 1.7 dm^3 lead(II) nitrate solution and was designed to conform to specified standards to achieve complete and uniform mixing of particles at a constant power number of 9.5 (Furusawa and Smith 1973, 1974; McKay and Allen 1980). Several experiments were performed in duplicate when identical concentration versus time curves were obtained.

TABLE 1.   Equipment Specification for Batch Adsorption Studies

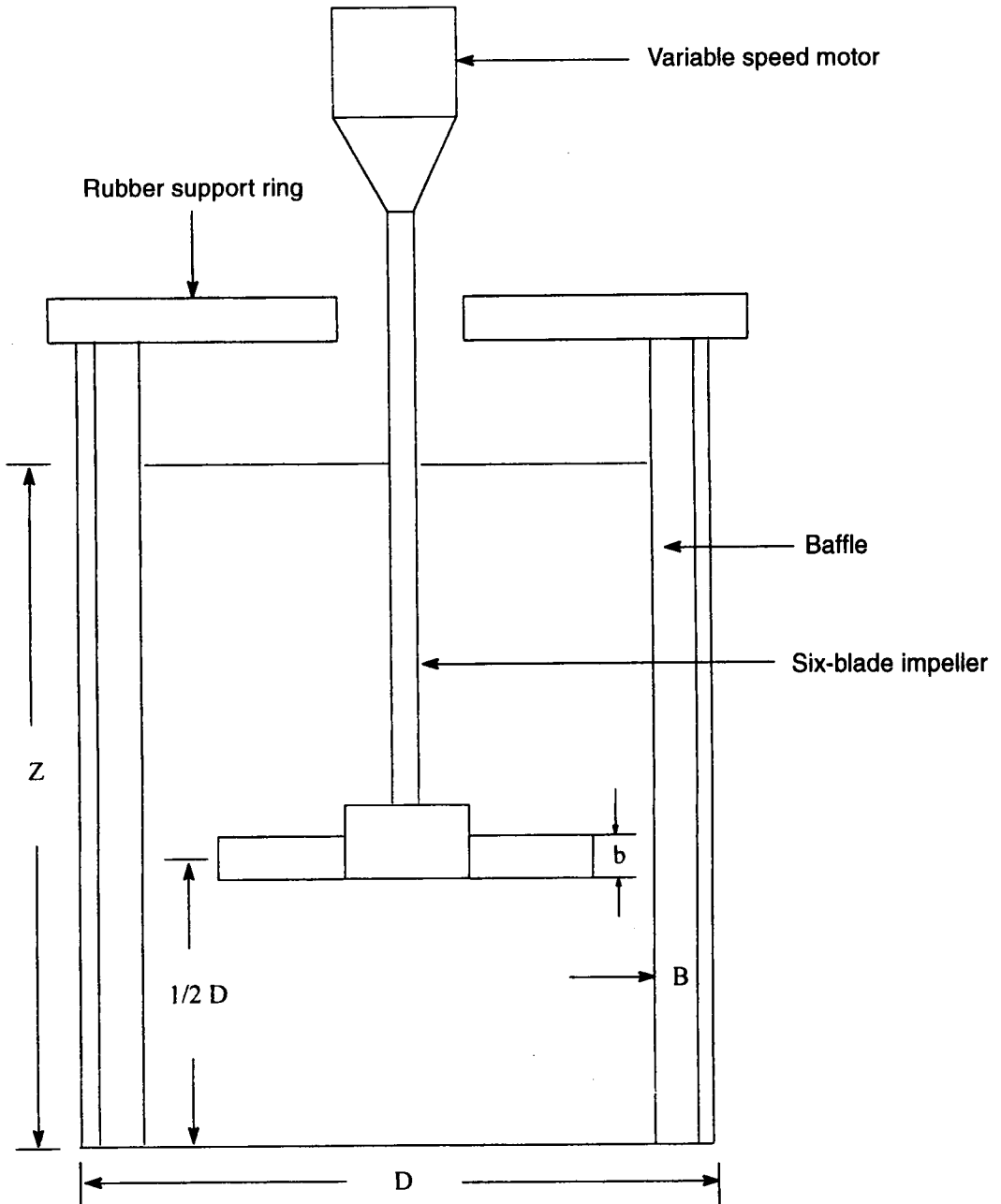| Description	Dimensions
Vessel diameter (14 cm)	D
Height of baffles	1.2D
Width of baffles (B)	(3/40)D
Height of liquid (Z)	D
Height of impeller from bottom of vessel	D/2
Width of blade of impeller (b)	D/10
Impeller diameter	D/2
Impeller shaft diameter	D/10

Figure 1. Schematic representation of sorber vessel.

Samples (3 ml) were withdrawn at suitable time intervals, filtered through a 0.45 μm membrane filter and then analysed with an inductively coupled plasma atomic emission spectroscopy analyser (ICP-AES) for all the studies. A 6.8 g sample of peat (500–710 μm) was added to each 1.7 dm³ batch volume of lead(II) solution using an agitation speed of 400 rpm at 24 ± 2°C. The solutions were adjusted to a pH of 4.5 using nitric acid.

RESULTS AND DISCUSSION

In a batch sorption process, the sorbent is contacted with the solution in a tank for a period of time under fixed operation conditions. The sorbent is then separated from the mix by settling, filtration or centrifugation and then regenerated or discarded. The time required to approach equilibrium depends on the concentration of sorbate, the dose of sorbent, the particle size of the sorbent, the degree of agitation, the temperature and the pH value.

Figure 2 shows a plot of the batch contact time data in the form of the amount of lead adsorbed per gram of peat versus time. At the three low concentrations studied, viz. 101, 209 and 309 mg/dm³, the equilibrium times were 10, 30 and 90 min, respectively. The two higher initial concentrations (410 mg/dm³ and 504 mg/dm³) reached equilibrium within 210 min under the same conditions of pH (4.5), temperature (24°C), agitation (400 rpm) and solution volume/sorbent mass ratio (0.25 dm³/g). Hence, equilibrium was achieved in 160 min for the case study conditions selected in this research using an initial lead concentration of 410 mg/dm³, a volume/mass ratio of 0.25 dm³/g and employing other experimental conditions as mentioned above.
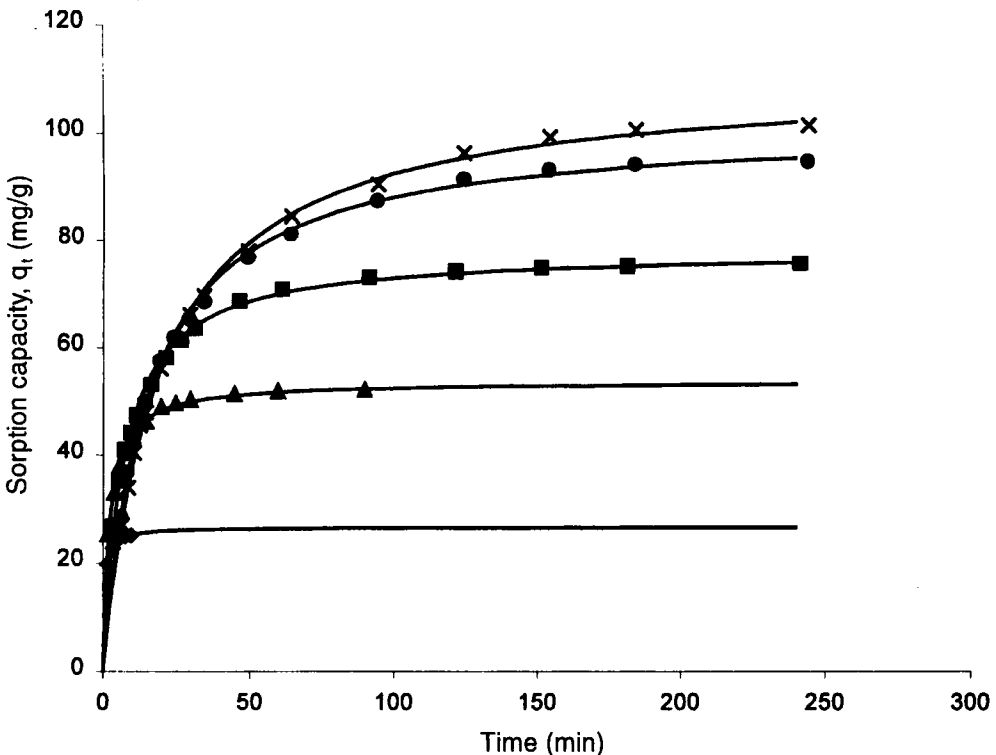

Figure 2. Plot of sorbed amount versus time for lead(II) at various initial concentrations: modified model, —; experimental data: ◆, C_0 = 101 mg/dm³; ▲, C_0 = 209 mg/dm³; ■, C_0 = 309 mg/dm³; ●, C_0 = 410 mg/dm³; ×, C_0 = 504 mg/dm³.

The mechanism for the process is based on the general concept that a divalent metal ion might be involved in an attachment to two carboxylate groups in humic acid with the release of two hydrogen ions, resulting in the observed decrease in pH of the solution. Several researchers have proposed the mechanism of sorption on to peat as a reaction between carboxylic groups in humic and fulvic acids with divalent metal ions (Schnitzer 1978; Boyd *et al.* 1981). These authors consider the mechanism as one of chelate ring formation involving adjacent carboxylate and phenolic hydroxy groups with the divalent metal ion. Stevenson and Chen (1991) determined the stability constants for copper–humate complexes based on binding at two sites. Spark *et al.* (1997) proposed that copper(II) has a potential to form cross-linked spherocolloids involving the carboxylate functional groups.

Many attempts have been made to explain the mechanism in terms of ionic effects using hydrogen ion titrations (Horst *et al.* 1990; Davis and Leckie 1980). However, in the case of humic substances, such methods have to overcome the extensive range of interactions between the charged surfaces of suspended colloids in solution and have proved to be extremely difficult to conduct (Dzombak and Morel 1990; Bartschat *et al.* 1992). The interactions and complexation reactions have been the subject of a detailed review (Buffle 1988). More recent structured studies by Francioso *et al.* (1996), using IR, Raman and NMR spectroscopic evidence, again supported a metal ion complex involving the carboxylic acid group. The authors concluded that the presence of a greater number of carboxylate and phenolic groups can explain the high affinity of peat for metal ions.

In other recent work, NMR and FT-IR structural studies were performed by Averett *et al.* (1998) on copper binding with carboxylate groups on humic and fulvic acid. These authors concluded that an inner-sphere complex of the metal binding fraction occurred based on chemisorption in which the copper ions were not irreversibly bound, with an outer-sphere binding complex being also formed. The model described here is based on one pseudo second-order rate constant which is used successfully to represent the several complex reactions taking place. The evidence presented in this discussion does, however, support the likelihood that the bonding is between carboxylate and phenolic hydroxys with divalent metal ions. A second-order reaction with respect to peat is a reasonable simplifying assumption, i.e.

$$2 \text{ peat} + Pb^{2+} \rightarrow (\text{peat})_2 Pb + 2H^+ \tag{1}$$

The schematic diagram for a multi-stage sorption system is shown in Figure 3. The solution to be treated contains L dm^3 solution and the lead(II) concentration is reduced for each stage from C_{n-1} to C_n mg/dm^3. The amount of peat added is S g with a lead(II) concentration on the peat of q_0 mg/g and the lead(II) concentration on the peat is increased from q_0 to q_n mg/g of peat. The mass balance equation gives:

$$L(C_{n-1} - C_n) = S(q_n - q_0) \tag{2}$$

The rate equation for a pseudo second-order chemical sorption process may be written as:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{3}$$

where q_e (mg/g) is the amount of lead(II) sorbed at equilibrium, q_t (mg/g) is the amount of lead(II) sorbed at time t and k [g/(mg min)] is the equilibrium rate constant for the pseudo second-order sorption process. Assuming that $q_t = 0$ at $t = 0$, the integrated form of equation (3) becomes:

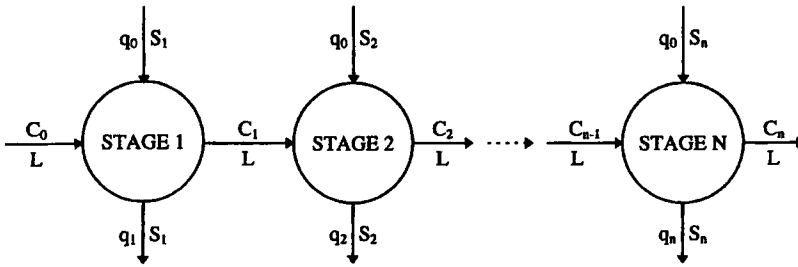$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \tag{4}$$

Figure 3.   Schematic for multi-stage countercurrent batch sorption.

Equation (4) can be rearranged to obtain:

$$q_t = \cfrac{t}{\left(\cfrac{1}{kq_e^2} + \cfrac{t}{q_e} \right)} \tag{5}$$

Equation (5) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \tag{6}$$

A kinetic analysis of the sorption of lead on peat has been tested according to the pseudo second-order equation. Figure 4 shows a plot of equation (6) for the sorption of lead(II) using peat. The results demonstrate a highly significant linear relationship between the lead(II) ions sorbed, t/q_t, and t in these studies with high correlation coefficients. Values of the correlation coefficients, r^2, the pseudo second-order rate parameters, k, and the sorption capacity, q_e, are listed in Table 2.

TABLE 2.   Parameters for Effect of Initial Concentration

C_o (mg/dm^3)	r^2	q_e (mg/g)	k [g/(mg min)]
101	1.000	27.0	5.15×10^{-2}
209	1.000	53.6	8.12×10^{-3}
309	1.000	77.29	2.25×10^{-3}
410	0.999	98.5	1.01×10^{-3}
504	0.998	106	7.62×10^{-4}

When fresh peat was used at each stage and the pseudo second-order rate expression employed to describe equilibrium in a multi-stage sorption system, then the mass balance equation may be obtained by combining equations (2) and (5):

$$C_n = C_{n-1} - \frac{Skq_n^2 t}{L(1 + kq_n t)} \tag{7}$$

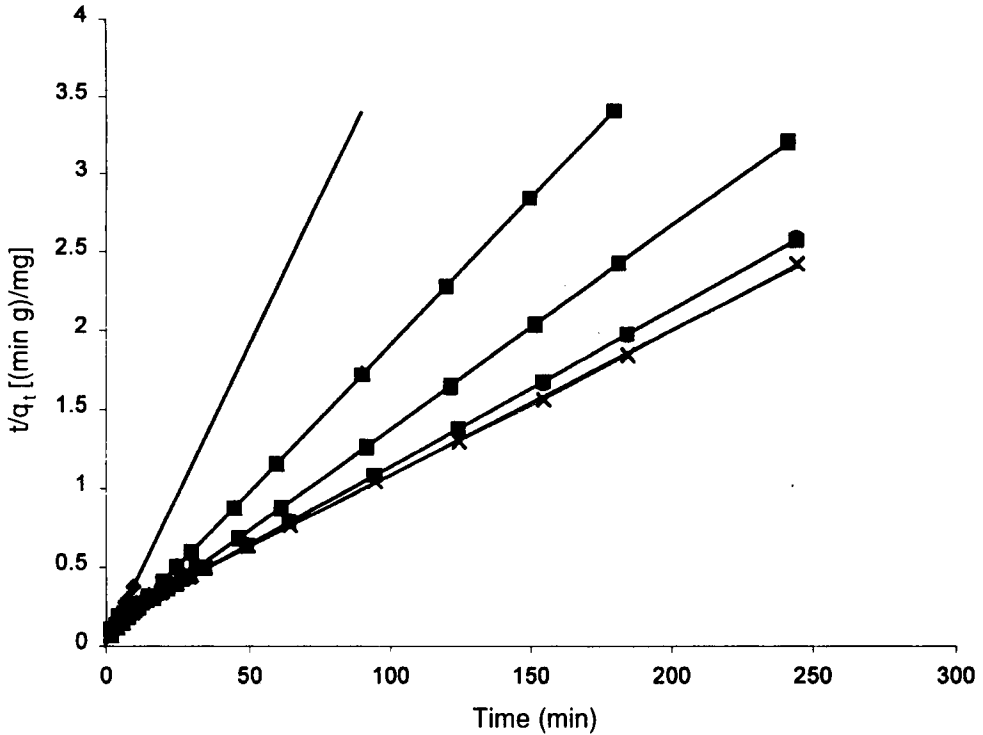The total amount of lead(II) removal can be calculated analytically as follows:

Figure 4. Pseudo second-order sorption kinetics of lead(II) on to peat at various concentrations: modified model, —; experimental data: ◆, $C_0 = 101$ mg/dm³; ▲, $C_0 = 209$ mg/dm³; ■, $C_0 = 309$ mg/dm³; ●, $C_0 = 410$ mg/dm³; ×, $C_0 = 504$ mg/dm³.

$$\sum_{n=1}^{n}(C_{n-1} - C_n) = \sum_{n=1}^{n}\frac{Skq_n^2 t}{L(1 + kq_n t)} \tag{8}$$

The lead(II) removal, R_n, in each stage can be evaluated from the equation as follows:

$$R_n = \frac{100(C_{n-1} - C_n)}{C_0} = \frac{100Skq_n^2 t}{LC_0(1 + kq_n t)} \tag{9}$$

The total removal of lead(II) can be determined analytically:

$$\sum_{n=1}^{n}R_n = \frac{100St}{LC_0}\sum_{n=1}^{n}\frac{kq_n^2}{1 + kq_n t} \tag{10}$$

The corresponding linear plots of the values of q_c and k versus C_0 were regressed to obtain expressions for these values in terms of the initial lead(II) concentration with high correlation coefficients (< 0.993). Hence it is further considered that q_c and k can be expressed as a function of C_0 for lead ions as follows:

$$q_c = 0.487C_0^{0.877} \tag{11}$$

$$k = 1.45 \times 10^4 C_0^{-2.72} \tag{12}$$

Substituting the values of q_e and k from equations (11) and (12) into equations (9) and (10) allows these two latter equations to be represented as follows:

$$R_n = \frac{100St(1.45 \times 10^4 C_{n-1}^{-2.72})(0.487 C_{n-1}^{0.877})^2}{LC_0[1 + (1.45 \times 10^4 C_{n-1}^{-2.72})(0.487 C_{n-1}^{0.877})\, t]} \tag{13}$$

$$\sum_{n=1}^{n} R_n = \frac{100St}{LC_0} \sum_{n=1}^{n} \frac{(1.45 \times 10^4 C_{n-1}^{-2.72})(0.487 C_{n-1}^{0.877})^2}{[1 + (1.45 \times 10^4 C_{n-1}^{-2.72})(0.487 C_{n-1}^{0.877})\, t]} \tag{14}$$

Equations (13) and (14) can be used for predicting the removal of lead(II) at any given initial lead ion concentration and the reaction time for multi-stage systems can be determined.

Consider the case of two-stage countercurrent batch sorption, when the solution to be treated contained 5 m³ solution, the amount of peat added was 20 kg in each of the two stages and the initial lead(II) concentration was 400 mg/dm³ in the first stage. Figure 5 shows a comparison of the
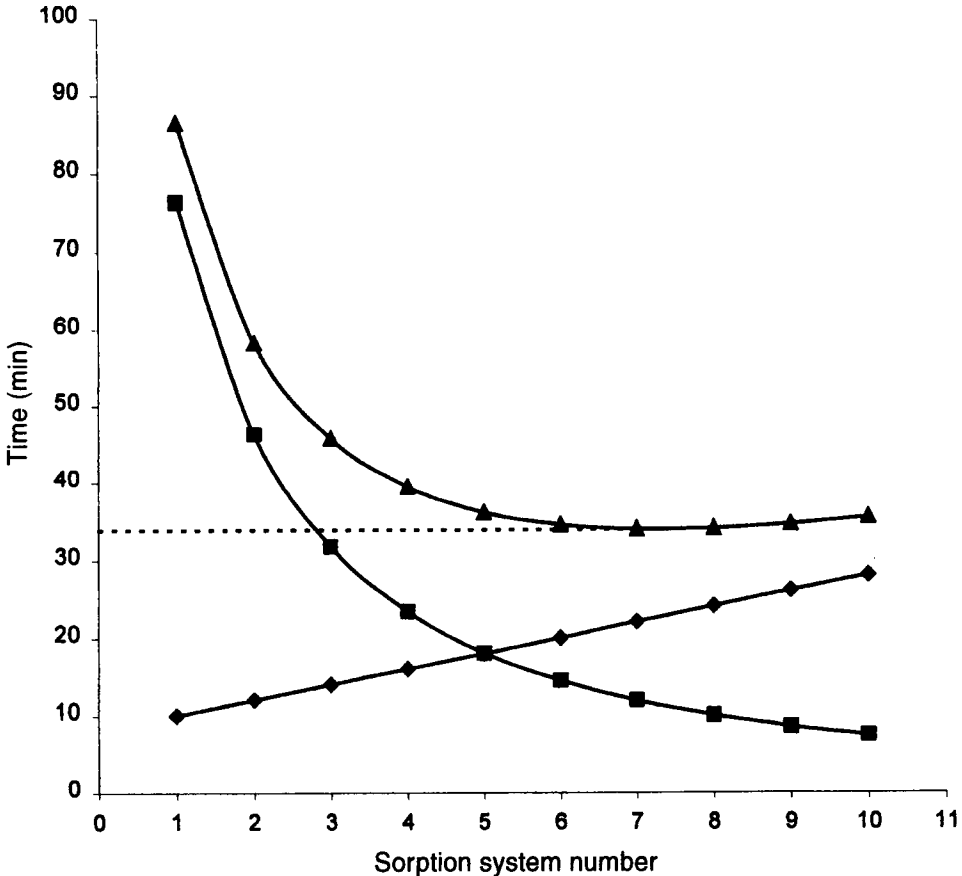

Figure 5. Comparison of 99% lead(II) removal time of each stage in a two-stage process: —◆—, stage 1; —■—, stage 2; —▲—, stage 3.

time for 99% lead(II) removal for each stage and the total reaction time of the two-stage counter-current batch sorption process. Figure 5 also shows the reaction time for a set of 10 two-stage sorption systems in series for each individual stage and for the combined total of the two stages. Each of the 10 systems representing the x-axes in Figures 5 and 6 were based on a 2-min contact time interval in the first adsorber starting with system 1 at 10 min. Thus, system numbers 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 represent contact times, t_1, in the first-stage sorber of 10, 12, 14, 16, 18, 20, 22, 24, 26, 28 min, respectively. Hence, the contact time in the second adsorber, t_2, is the total contact time required, T, to achieve a specified overall percentage dye removal minus the contact time in the first adsorber, i.e.:

$$t_2 = T - t_1 \tag{15}$$

Table 3 shows a series of sorption systems for testing, the minimum operation time for various percentage lead(II) removal in a two-stage process being evaluated from equation (13) for each system. Figure 6 shows the minimum contact time for various percentage lead(II) removal values in a two-stage process. The minimum contact time for 99% lead(II) removal can be found using equation (13) or by plotting graphs analogous to Figure 6. For 99% lead(II) removal, the minimum contact time is 33.9 min as shown by system 7 with reaction times of 22 min for stage 1 and 11.9 min for stage 2; for 98% lead(II) removal the minimum time is 31 min as shown by system 5 with reaction times of 18.1 min for stage 1 and 13.0 min for stage 2; for 96% lead(II) removal the time is 26.1 min; for 94% lead(II) removal the time is 23.0 min; and for 92% lead(II) removal the time is 20.7 min.

TABLE 3. Reaction Time (min) for a Series Sorption System

System No.	Stage 1	Stage 2 99% removal	Stage 2 98% removal	Stage 2 96% removal	Stage 2 94% removal
1	10	76.4	45.8	24.7	16.5
2	12	46.3	30.3	17.4	11.9
3	14	31.7	21.8	13.0	8.98
4	16	23.4	16.5	10.1	7.02
5	18	18.1	13.0	8.06	5.64
6	20	14.5	10.5	6.60	4.63
7	22	11.9	8.74	5.51	3.87
8	24	9.99	7.38	4.68	3.29
9	26	8.54	6.34	4.03	2.83
10	28	7.40	5.51	3.50	2.46

CONCLUSIONS

The design model presented is based on a pseudo second-order equation and this has been used for minimising the reaction time used in a two-stage contact system. The model has been optimised with respect to contact time in order to minimise total contact time to achieve a fixed percentage of metal ion removal using a fixed mass of sorbent. It is particularly suitable for low-cost sorbents sorption systems when minimising contact time is a major operational and design criterion — such
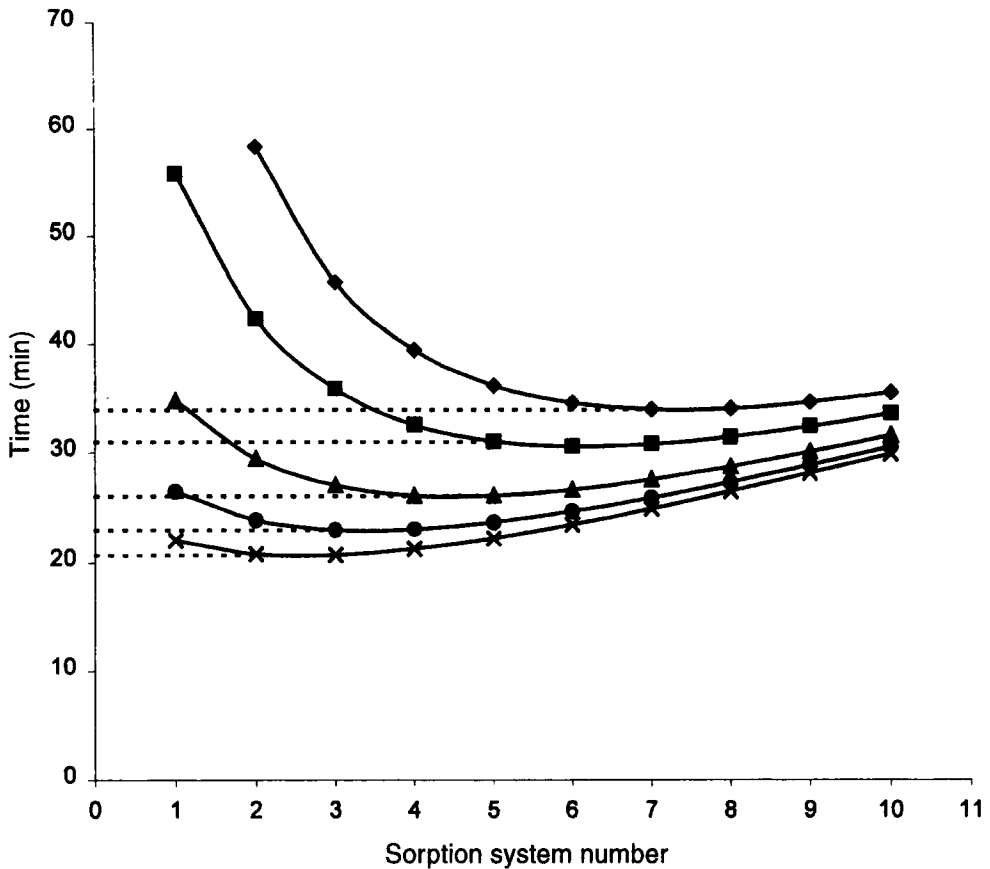
Figure 6. Minimum contact time for various percentage lead(II) removal in a two-stage process: —◆—, 99% removal; —■—, 98% removal; —▲—, 94% removal; —×—, 92% removal.

as for highly congested industrial sites in which significant volumes of effluent need to be treated in the minimum amount of time.

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