A branched pore kinetic model applied to the sorption of metal ions on bone char

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Abstract: A slightly modified form of the branched pore model of Peel, Benedek and Crowe was successfully applied to describe the batch sorption kinetics of three metal ions—cadmium, copper and zinc—on bone char. In comparison with an analytical film-surface solution, the additional parameters of the branched pore model were observed to produce a significant improvement in correlating the experimental results. The ranges of the values of the model parameters derived were deemed reasonable and the branched pore sorption capacities of two of the three metal ions were comparable (ca. 0.16 mmol g\(^{-1}\)). Given that the surface diffusivities of the metal ions were observed to vary with averaged surface loading, a number of correlations were examined for their accuracy in describing this behaviour. The exponential expression of Neretnieks resulted in the smallest total error when the data for all three metal ions were considered together.

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Keywords: branched pore; bone char; surface diffusion

NOTATION

- \( b \): Langmuir/Sips isotherm parameter (dm\(^3\) mg\(^{-1}\))
- \( C \): Liquid phase concentration in the bulk solution (mg dm\(^{-3}\))
- \( C_{\text{cal}} \): Model-derived liquid phase concentration (mg dm\(^{-3}\))
- \( C_e \): Equilibrium solute concentration in the liquid phase (mg dm\(^{-3}\))
- \( C_{\text{exp}} \): Experimentally measured liquid phase concentration (mg dm\(^{-3}\))
- \( C_r \): Liquid phase concentration at the particle surface (mg dm\(^{-3}\))
- \( C_0 \): Initial liquid phase concentration in the bulk solution (mg dm\(^{-3}\))
- \( C_1 \): Liquid phase concentration in the first sample (mg dm\(^{-3}\))
- \( D_b \): Surface diffusion coefficient (cm\(^2\) s\(^{-1}\))
- \( D_{b0} \): Surface diffusion coefficient at zero loading (cm\(^2\) s\(^{-1}\))
- \( f \): Fraction of total solid phase capacity contributed by macropores (dimensionless)
- \( i \): Radial grid index (dimensionless)
- \( j \): Temporal grid index (dimensionless)
- \( k \): Sample number (dimensionless)
- \( k_b \): Branched pore rate transfer parameter (s\(^{-1}\))
- \( k_t \): Liquid film mass transfer coefficient (cm s\(^{-1}\))
- \( m \): Mass of adsorbent (g)
- \( n \): Exponential parameter in the Sips isotherm (dimensionless)
- \( NR \): Number of radial grid divisions (dimensionless)
- \( NS \): Number of liquid samples (dimensionless)
- \( NT \): Number of temporal grid divisions (dimensionless)
- \( q \): Amount adsorbed (mg g\(^{-1}\))
- \( q_{b,r} \): Solid phase concentration in the adsorbent branched pores at radius \( r \) (mg g\(^{-1}\))
- \( q_e \): Equilibrium solute concentration in the adsorbed phase (mg g\(^{-1}\))
- \( q_{m,r} \): Solid phase concentration in the adsorbent macropores at radius \( r \) (mg g\(^{-1}\))
- \( q_{n,R} \): Solid phase concentration evaluated at \( r = R \)
- \( q_s \): Solute concentration in the adsorbed phase at saturation (mg g\(^{-1}\))
- \( \hat{q} \): Volume averaged solid phase concentration (mg g\(^{-1}\))
- \( Q_{\text{st},a} \): Apparent isosteric heat of adsorption (J mol\(^{-1}\))
- \( Q_0 \): Constant defined by the equation \( Q_{\text{st},a} = -Q_0 \cdot \ln(\psi \cdot q) \) (J mol\(^{-1}\))
- \( r \): Radial position within the adsorbent particle (cm)
- \( R \): External radius of the adsorbent particle (cm)
- \( t \): Time (s)
- \( t_k \): Time when liquid sample was taken (s)
- \( t_0 \): Time when initial sample was taken (\( t = 0 \)) (s)

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INTRODUCTION

The discharge of heavy metals such as copper, zinc and cadmium from the microelectronics and electroplating industries is still a significant environmental problem in many areas. Sorption processes offer a potentially lower cost alternative to ion exchange for removing metal ions from low and medium concentration effluents. A number of sorbents have been tested for copper, cadmium and zinc removal, including carbon, chitosan, goethite, peat, bone char and agricultural waste. Several studies have also been carried out using biomass materials, such as algae, fungi, plants and microorganisms. The uptake of solute by an adsorbent may involve two parallel mass-transfer mechanisms, pore and surface diffusion. Pore diffusion is driven by a concentration gradient within the fluid in the pore and the diffusion coefficient typically does not exhibit concentration dependence. Surface diffusion occurs along the surface of the pore and is driven by the concentration gradient in the adsorbed phase. Experimentally-derived surface diffusivities have been shown to vary with solid phase concentration. Conceptually, this can be explained if the process of surface diffusion occurs through adsorbates hopping from site to site with an activation energy that is related to the heat of adsorption. For a surface that has a distribution of sites of different energies, mobility will increase with surface coverage if the most strongly binding/adsorbing sites are occupied first. Based on this mechanism, Higashi et al derived an expression in which the surface diffusion coefficient varied inversely with the fraction of the surface remaining uncovered. By using different functions to describe the distribution of adsorption site energies, relationships between the heat of adsorption and surface coverage—and thus surface diffusion—can be derived, eg assuming a linear relationship, exponential dependence or power-law dependence. Other fundamental approaches have derived thermodynamically consistent expressions for surface diffusivity as a function of surface coverage, the most commonly quoted is that of Darken. In his study of interdiffusion in metal alloys, Darken determined that the surface diffusivity at any loading could be described by the value at zero loading multiplied by a thermodynamic correction factor, derived based on chemical potential and given by the gradient of the log of the fluid phase concentration versus the log of the solid phase concentration. The extensive use of his approach is due to the close relationship of the expression to the equilibrium isotherm—e.g. for systems where the sorption equilibrium can be represented by the Langmuir isotherm, the Darken equation is identical to that of Higashi et al’s model. Comprehensive review articles by Kapoor et al and Choi et al are recommended for those interested in more detailed analysis of concentration dependence in surface diffusion.

Systems which take a long time to reach equilibrium may be influenced by more than one diffusion process. While bimodal diffusion models are commonly applied in modelling sorption on molecular sieves, lumped parameter approaches are more often used with heterogeneous adsorbents, such as activated carbons. One of the few models that has attempted to develop beyond the single lumped parameter is the branched pore kinetic model of Peel and co-workers. This model incorporates three mass transfer parameters—an external film resistance, a surface diffusion coefficient and a composite rate parameter, which determines transport from the macropores to the branched pores—and divides the adsorption capacity of the particle into two sections: a fraction, \( f_i \) in the macropores and the remaining fraction, \( (1 - f) \), in the branched pores. Relatively rapid diffusion occurs in the macropores and the remaining slow approach to equilibrium occurs through the combined effect of the composite rate parameter, restricting transport into the branched pores, and diffusion within the branched pores.

In this paper, we have applied a modified form of the branched pore model to describe the sorption of metal ions on a complex heterogeneous adsorbent, bone char, and have examined, and attempted to correlate, the variation of surface diffusivity with adsorbent loading.

EXPERIMENTAL

Adsorbent

The bone char used in this study was Brimac 216, 20/60 mesh supplied by Tate & Lyle Process Technology. The main component of bone char is...
The initial and final concentrations of the solutions of 
the adsorbates were adjusted to 5

Sulfuric acid is commonly used to acidify plating 
and other similar processes in industry and 
thus wastewaters usually contain sulfate ions in solution. 
Analytical grade cadmium sulfate (CdSO₄·8H₂O) and 
copper(II) sulfate (CuSO₄·5H₂O) from Riedel-de Hahn Chemicals, 
and analytical grade zinc sulfate (ZnSO₄·7H₂O) from 
BDH chemicals were used to prepare stock metal ion solutions in deionized water.

The concentrations of metal ion solutions were measured using an Inductively Coupled Plasma- 
Atomic Emission Spectrometer (ICP-AES). The samples were diluted five times by deionized water 
to ensure that measured values remained within the 
linear range of the instrument. Typically, each sample was measured three times in one aspiration. If the standard deviation of test results was greater than 2%, 
repeat measurements were made until the test results comply with this standard.

The rate of intraparticle mass transfer within the 
macropores is modelled based on a modified surface 
diffusion equation for spherical particles:

\[ f \cdot \frac{\partial q_{m,r}}{\partial t} + (1-f) \cdot \frac{\partial q_{b,r}}{\partial t} = f \cdot \frac{D_s}{r^2} \cdot \frac{\partial}{\partial r} \left( r^2 \cdot \frac{\partial q_{m,r}}{\partial r} \right) \]

The fits of the resulting equilibrium data to two 
isotherm equations were evaluated.
where:

$$\frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q_{m,r}}{\partial r} \right) = D_s \left( \frac{\partial^2 q_{m,r}}{\partial r^2} + \frac{2}{r} \frac{\partial q_{m,r}}{\partial r} \right)$$

and the rate of transport to the branched pore region is modelled as a first-order rate process:

$$\left( 1 - f \right) \frac{\partial q_{b,r}}{\partial t} = k_b \cdot (q_{m,r} - q_{b,r})$$

which eqn (5) is undefined at the centre of the adsorbent and can only be incorporated after modification. Applying the internal boundary condition, eqn (10), and eqn (11) to be solved at the fluid–solid interface. The final set of algebraic equations—eqns (11), (12), (13) and (14)—can thus be solved by matrix inversion. However, since the right-hand side of eqn (14) depends on values of $C$ and $C_R$ that are not known at the current time-step, iterative convergence is necessary before moving to the next time-step and repeating the solution process.

Having subsequently determined values for $NR$ and $NT$ which result in stable and converged solutions, the final development of the model was to incorporate it within a simplex optimization procedure to determine the best-fit set of model parameters—$k_b$, $D_s$, $k_b$ and $f$—to simulate the concentration decay curves determined from batch sorption experiments. In all cases the goodness-of-fit was determined based on the sum of the squares of the errors (SSE) between the experimentally measured bulk solution concentration values and those calculated by the model at the same measurement times:

$$SSE = \sum_{k=1}^{NS} (C_{exp}(t_k) - C_{cal}(t_k))^2$$

RESULTS AND DISCUSSION

Equilibrium isotherms

The equilibrium isotherms were analysed using the Langmuir and Sips isotherms:

$$\text{Langmuir isotherm} : q_e = q_s \cdot \frac{b \cdot C_e}{1 + b \cdot C_e}$$

$$\text{Sips isotherm} : q_e = q_s \cdot \left( \frac{b \cdot C_e}{1 + (b \cdot C_e)^{1/\alpha}} \right)$$

The best-fit isotherm equation was determined for each metal ion–bone char system based on a comparison of the model and experimental SSE values. The copper and cadmium ion systems showed a better fit when the Sips isotherm was used and the zinc ion system gave a better fit when using the

† The model and associated input files can be downloaded from http://ihome.ust.hk/~kejep (valid until 1st June 2005).
Table 1. Equilibrium isotherm parameters for copper, cadmium and zinc ions on bone char

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>$q_s$ (mg g$^{-1}$)</th>
<th>$b$ (dm$^3$ mg$^{-1}$)</th>
<th>$1/n$</th>
<th>SSE ($q_e$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>79.284</td>
<td>0.0736</td>
<td>0.4038</td>
<td>266.064</td>
</tr>
<tr>
<td>Copper</td>
<td>62.169</td>
<td>0.2305</td>
<td>0.4416</td>
<td>217.159</td>
</tr>
<tr>
<td>Zinc</td>
<td>30.216</td>
<td>0.4964</td>
<td>1.0</td>
<td>356.988</td>
</tr>
</tbody>
</table>

Langmuir isotherm. Since the surface of the bone char is known to be heterogeneous, the isotherm fit should not be regarded as having mechanistic significance. A summary of the isotherm constants derived is given in Table 1.

Application of the branched pore surface diffusion model

In order to find best-fit sets of the model parameters, the optimization procedure required initial values to be provided. An initial estimate for the external mass transfer coefficient was determined from a simplified numerical approximation to a film transfer model over the first two data points:

$$k_f \approx -\frac{2}{3} \cdot \frac{V \cdot \rho_p \cdot r}{m \cdot (t_0 - t_1)} \cdot \left( \frac{C_0 - C_1}{C_0 + C_1} \right)$$

and an initial estimate for the surface diffusivity was derived from an analytical solution for film plus surface diffusion into a spherical particle.

The branched pore model was initially used to determine a set of the four parameters for each concentration decay curve and a mean value was then taken for each of the parameters for each of the three metal ion–bone char systems. The model was then executed with these averaged parameter values and cumulative SSE values were determined for the experimental data for each metal ion system. The values of the four model parameters for the sorption of copper, cadmium and zinc ions on bone char are shown in Table 2. The effects of initial metal ion concentration and sorbent mass for cadmium, copper and zinc ions using the averaged parameter values are illustrated in Figs 1–3.

In terms of the actual parameter values determined, the values for $k_f$ appear reasonable in terms of order of magnitude. Compared with values estimated using

Table 2. Constant mass transfer parameters ($k_f$, $D_s$, $k_b$ and $f$) for the adsorption of metal ions on bone char

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>$m$ (g)</th>
<th>$C_0$ (mg dm$^{-3}$)</th>
<th>$k_f$ (cm s$^{-1}$)</th>
<th>$D_s$ (cm$^2$ s$^{-1}$)</th>
<th>$k_b$ (s$^{-1}$)</th>
<th>$f$ (dimensionless)</th>
<th>SSE ($C_t$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>242</td>
<td>2948.5</td>
<td>1857.1</td>
<td>97.0</td>
<td>1012.1</td>
<td>7315.0</td>
<td>14 245.2</td>
</tr>
<tr>
<td>Copper</td>
<td>134</td>
<td>1157.5</td>
<td>773.8</td>
<td>121.7</td>
<td>1778.9</td>
<td>1403.2</td>
<td>5815.5</td>
</tr>
<tr>
<td>Zinc</td>
<td>148</td>
<td>2843.4</td>
<td>1390.3</td>
<td>123.7</td>
<td>2301.0</td>
<td>3880.7</td>
<td>11 647.2</td>
</tr>
</tbody>
</table>

a common correlation, e.g. Harriott’s correlation,26 the values shown here are 20–40% smaller than expected and there seems to be no significant correspondence between \( k_f \) and the molar diffusivity of the ions. The values determined for \( k_b \) are comparable to recent published values,27,28 although significantly larger than those presented in the original branched pore paper22 and others derived from it.29,30 The discrepancy with earlier published results may be related to the constants used in the non-dimensional form of the intraparticle diffusion equation. The fraction of total adsorption capacity in macropores, \( f \), is within an acceptable range (between 0 and 1), and the molar values of the branched pore capacities—i.e. \((1 - f) \times q_s\)—for two of the metal ions are quite similar (0.076, 0.180 and 0.151 mmol g\(^{-1}\) respectively, for cadmium, copper and zinc). The values of the surface diffusivity in the fixed case are also reasonable—having a similar order of magnitude to those of heavy metals on ion exchange resins.31

If a constant \( D_s \) value is used in the model, the effect of surface loading at any given time will be ignored. The previous results shown in Table 2 show that the largest errors are typically associated with dynamic sorption curves for the lowest and highest initial concentrations for all three metal ion systems, suggesting that \( D_s \) may in fact change with surface coverage. Since previous research has also established that surface diffusivity can vary with liquid concentration and thus surface loading,14–17,32–35 in the second application of the model, three of the mass transport parameters (\( k_f \), \( k_b \) and \( f \)) were kept constant while \( D_s \) was allowed to vary. Table 3 and Figs 4–6 show the model results based on a variable surface diffusivity. The SSE values determined using a variable \( D_s \) are much smaller than those obtained from an averaged \( D_s \). The largest improvement was observed for the cadmium ion system, where the total SSE value for all the decay curves decreased from 14 252.2 to 1048; the cumulative SSEs for the copper and zinc systems decreased by factors of 3 and 12 times respectively. As can be seen from the results, in each case the largest improvements were observed for decay curves measured at extreme values of initial
concentration. Table 3 lists the final parameter sets that would be recommended for use and Table 4 provides a simple linear fit to enable others to estimate a suitable value for \( D_s \) based only on the initial experimental conditions.

Prior to further analysis of the data, the results from the branched pore surface diffusion model were compared with results from an analytical film plus surface diffusion model, and comparison of the two models is given in Table 5 and Fig 7. It was found that the data fittings provided by the branched pore model resulted in a significant reduction in SSE values (e.g., a four-fold reduction was observed for zinc) when compared with the two-parameter analytical solution, supporting using the more complex four-parameter branched pore diffusion model to describe mass transport within the bone char particle.

Figure 6. Effect of sorbent mass on the adsorption of zinc ions on bone char \( (C_0 = 220 \text{ ppm}) \) with variable \( D_s \) and constant \( k_f, k_b \) and \( f \).

Figure 7. Comparison of sample data fittings based on a two resistance (analytical film plus surface) diffusion model and the branched pore kinetic model.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>( m ) (g)</th>
<th>( C_0 ) (mg dm(^{-2}))</th>
<th>( k_f ) (cm s(^{-1}))</th>
<th>( D_s ) (cm(^2) s(^{-1}))</th>
<th>( k_b ) (s(^{-1}))</th>
<th>( f ) (dimensionless)</th>
<th>SSE (C(_t))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>242</td>
<td>3.58 \times 10^{-9}</td>
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</tr>
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<td>Total SSE</td>
<td></td>
<td>1570.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total SSE</td>
<td></td>
<td>913.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Surface diffusivity correlations
Given that significant reductions in SSEs were obtained when $D_s$ was allowed to vary and that the value of $D_s$ was seen to increase with surface coverage, the observed behaviour of the systems would appear to be qualitatively acceptable. Several functions, based on either a thermodynamic correction factor or an energy distribution for activated sorption, were examined in an attempt to correlate $D_s$ with averaged fractional surface coverage. Since the present work was performed isothermally, temperature dependence was not examined.

Model 1—the Higashi Ito Oishi expression\textsuperscript{14}
This is identical to the Darken thermodynamic correction factor for the Langmuir isotherm, ie:

$$\frac{D_s}{D_{s0}} = \left(\frac{q_e}{C_0}\right)^{\frac{\partial \ln(C_e)}{\partial \ln(q_e)}} = \left(\frac{q_e}{C_e}\right)^{\frac{\partial C_e}{\partial q_e}}$$

$$= \frac{q_e}{q_s - q_e} = \frac{1}{1 - \theta}$$

and is of a similar form to the thermodynamic correction factor for the Sips isotherm:

$$D_s = D_{s0} \cdot n \cdot \left(\frac{1}{1 - \theta}\right)$$

Hence the general form of the expression is appropriate to both of the isotherms used.

Model 2—a power-law variation on Model 1
Unlike the Darken expressions for the Langmuir and Volmer isotherms\textsuperscript{36} in this case the exponent $\lambda$ is not restricted to an integer value and should be considered only as an empirical fitting parameter:

$$D_s = D_{s0} \cdot \left(\frac{1}{1 - \theta}\right)^\lambda$$

Model 3—a simplified version of the expression of Okazaki et al\textsuperscript{34,37}
Here the fitting parameter, $\tau$, depends on the ratio of the time spent in the second and outer layers over the time spent in the first layer of the adsorbed phase (ie the layer of adsorbed material closest to the adsorbent surface). A value greater than unity indicates that one or other of these so-called holding times is negative and, in such a case, the physical significance of the parameter can only be considered to be empirical:

$$D_s = D_{s0} \cdot \frac{1}{1 - \tau \cdot \theta}$$

Model 4—Neretniks’ exponential expression\textsuperscript{15}
This model was developed based on activated surface diffusion and assuming a linear change of heat of adsorption (and thus activation energy for diffusion) with surface loading:

$$D_s = D_{s0} \cdot \exp(\alpha \cdot \theta)$$

The non-dimensional parameter $\alpha$ is related to the difference in heat of adsorption between the highest energy (corresponding to the first surface site occupied) and lowest energy (ie last occupied) site.

Model 5—derived from Suzuki and Fuji’s power-law expression\textsuperscript{16}
Suzuki and Fuji correlated changes in surface diffusivity with the solid phase concentration for propanoic acid on carbon using a power-law relationship:

$$D_s = D_{s0} \cdot (\psi \cdot q)^n$$

Their derivation was based on activated surface diffusion and a logarithmic change of isosteric heat of adsorption with surface loading:

$$Q_{a.s} = -Q_0 \cdot \ln(\psi \cdot q)$$

### Table 4.
Linear equations which correlate $D_s$ for copper, cadmium and zinc ions on bone char based solely on initial conditions (where $C_0$ and $C_e$ have units of mg dm$^{-3}$ and $m$ has units of g)

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Slope</th>
<th>Intercept</th>
<th>Parameter</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>$8.3725 \times 10^{-11}$</td>
<td>$1.5038 \times 10^{-9}$</td>
<td>$C_0 / m$</td>
<td>0.7501</td>
</tr>
<tr>
<td>Copper</td>
<td>$2.5030 \times 10^{-11}$</td>
<td>$6.9374 \times 10^{-11}$</td>
<td>$C_0 - C_e$</td>
<td>0.8573</td>
</tr>
<tr>
<td>Zinc</td>
<td>$3.5463 \times 10^{-11}$</td>
<td>$-2.4181 \times 10^{-9}$</td>
<td>$C_0 - C_e$</td>
<td>0.9320</td>
</tr>
</tbody>
</table>

### Table 5.
Comparison of $D_s$ and SSE values obtained from an analytical film plus surface diffusion model and the branched pore kinetic model for the zinc ions

<table>
<thead>
<tr>
<th>m (g)</th>
<th>$C_0$ (mg dm$^{-3}$)</th>
<th>$D_s$ (cm$^2$ s$^{-1}$)</th>
<th>SSE (C$^2$)</th>
<th>$D_s$ (cm$^2$ s$^{-1}$)</th>
<th>SSE (C$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>148</td>
<td>$3.03 \times 10^{-9}$</td>
<td>82.5</td>
<td>$5.14 \times 10^{-9}$</td>
<td>30.7</td>
<td></td>
</tr>
<tr>
<td>182</td>
<td>$3.77 \times 10^{-9}$</td>
<td>39.2</td>
<td>$5.39 \times 10^{-9}$</td>
<td>114.8</td>
<td></td>
</tr>
<tr>
<td>8.5</td>
<td>$220$</td>
<td>$4.81 \times 10^{-9}$</td>
<td>24.8</td>
<td>$6.89 \times 10^{-9}$</td>
<td>197.3</td>
</tr>
<tr>
<td>286</td>
<td>$7.46 \times 10^{-9}$</td>
<td>148.1</td>
<td>$1.13 \times 10^{-8}$</td>
<td>320.6</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>$8.23 \times 10^{-9}$</td>
<td>239.6</td>
<td>$1.19 \times 10^{-8}$</td>
<td>1762.2</td>
<td></td>
</tr>
<tr>
<td>6.5</td>
<td>$4.98 \times 10^{-9}$</td>
<td>113.7</td>
<td>$7.03 \times 10^{-9}$</td>
<td>432.7</td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>$5.53 \times 10^{-9}$</td>
<td>27.6</td>
<td>$7.94 \times 10^{-9}$</td>
<td>294.0</td>
<td></td>
</tr>
<tr>
<td>8.5</td>
<td>$220$</td>
<td>$4.81 \times 10^{-9}$</td>
<td>24.8</td>
<td>$6.89 \times 10^{-9}$</td>
<td>197.1</td>
</tr>
<tr>
<td>9.5</td>
<td>$5.53 \times 10^{-9}$</td>
<td>52.0</td>
<td>$6.61 \times 10^{-9}$</td>
<td>105.8</td>
<td></td>
</tr>
<tr>
<td>10.5</td>
<td>$6.61 \times 10^{-9}$</td>
<td>186.1</td>
<td>$6.96 \times 10^{-9}$</td>
<td>35.3</td>
<td></td>
</tr>
</tbody>
</table>

Total SSE: 913.8 Total SSE: 4293.4
In the expression used here, the exponent is not restricted to being related to a Freundlich isotherm and $D_s$ is correlated with fractional surface coverage raised to some power, $\gamma$:

$$D_s = D_{s0} \cdot \theta^\gamma$$  \hspace{1cm} (23)

**Model 6—complex power-law expression**

Two alternative and purely empirical combinations of models 2 and 5:

(a)$D_s = D_{s0} \cdot \theta \cdot \left( \frac{1}{1 - \theta} \right)^\lambda$  \hspace{1cm} (24)

(b)$D_s = D_{s0} \cdot \theta \cdot \left( \frac{\theta}{1 - \theta} \right)^\lambda$  \hspace{1cm} (25)

**Summary of the correlation results for the three metals**

The ranges of averaged fractional surface coverage were found to be very similar for copper and cadmium and the scatter in both sets of data appear to contribute to the relatively high error values for most of the correlations. As can be seen from the data in Tables 6 and 7 however, model 1, the Higashi Ito Oishi expression, provided the worst fit by a significant margin for both metals. Given the heterogeneity of the bone char surface, this result should perhaps, not be surprising. The next worst fit was provided by the modified Okazaki expression and, as the values of the fitting parameter were greater than unity for both metal ions, the parameter values derived could only be considered empirical. Of the remaining correlations, the SSE values provide little to differentiate them, with model 5 and model 2 providing marginally worse fits for cadmium and copper respectively.

The data for zinc seemed to be more discriminatory in terms of model fits, since they were less affected by scatter and extended (at least in one direction) to more extreme values of averaged fractional surface coverage. In this case, from the results presented in Table 8, Neretnieks’ and the second form of complex power law expression provided comparable and accurate correlation of the diffusion coefficients.

Assuming that all three metal ions behave similarly in terms of transport and attachment processes within the bone char, the effect that surface loading has on their respective surface diffusion coefficients should also be similar. Following this line of reasoning, the cumulative total SSE values for all three metals for each correlation was examined for consistency with the observations for the individual metal ions. The smallest cumulative total SSE values were determined for model 6 (a: 115.96 × 10^{-20} cm^4 s^{-2}; b: 113.22 × 10^{-20} cm^4 s^{-2}) and model 4 (111.98 × 10^{-20} cm^4 s^{-2}).

It is accepted that the thermodynamic correction factor in Darken’s expression should tend to a finite non-zero value, generally unity, at low surface loadings $7^{19}$ implying that the Fickian transport diffusivity ($D_s$) should tend to the value of the corrected $D_s (cm^2 s^{-1})$

<table>
<thead>
<tr>
<th>Model</th>
<th>$D_{s0}$</th>
<th>$\alpha$</th>
<th>$\lambda$</th>
<th>$\gamma$</th>
<th>$\tau$</th>
<th>SSE ($\times 10^{20}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.8633 × 10^{-9}</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>455.49</td>
</tr>
<tr>
<td>2</td>
<td>1.2309 × 10^{-9}</td>
<td>—</td>
<td>2.32135</td>
<td>—</td>
<td>—</td>
<td>38.05</td>
</tr>
<tr>
<td>3</td>
<td>1.8165 × 10^{-9}</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.40016</td>
<td>47.53</td>
</tr>
<tr>
<td>4</td>
<td>0.6518 × 10^{-9}</td>
<td>4.50947</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>37.11</td>
</tr>
<tr>
<td>5</td>
<td>27.6829 × 10^{-9}</td>
<td>—</td>
<td>2.14331</td>
<td>—</td>
<td>—</td>
<td>44.56</td>
</tr>
<tr>
<td>6(a)</td>
<td>5.2343 × 10^{-9}</td>
<td>—</td>
<td>1.24619</td>
<td>—</td>
<td>—</td>
<td>36.89</td>
</tr>
<tr>
<td>6(b)</td>
<td>12.4796 × 10^{-9}</td>
<td>—</td>
<td>0.59801</td>
<td>—</td>
<td>—</td>
<td>39.71</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Model</th>
<th>$D_{s0}$</th>
<th>$\alpha$</th>
<th>$\lambda$</th>
<th>$\gamma$</th>
<th>$\tau$</th>
<th>SSE ($\times 10^{20}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.7309 × 10^{-9}</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>220.74</td>
</tr>
<tr>
<td>2</td>
<td>1.5179 × 10^{-9}</td>
<td>—</td>
<td>1.99825</td>
<td>—</td>
<td>—</td>
<td>71.06</td>
</tr>
<tr>
<td>3</td>
<td>1.8989 × 10^{-9}</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.37477</td>
<td>76.12</td>
</tr>
<tr>
<td>4</td>
<td>1.0075 × 10^{-9}</td>
<td>3.58056</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>67.67</td>
</tr>
<tr>
<td>5</td>
<td>17.5193 × 10^{-9}</td>
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<td>1.54858</td>
<td>—</td>
<td>—</td>
<td>66.79</td>
</tr>
<tr>
<td>6(a)</td>
<td>7.3569 × 10^{-9}</td>
<td>—</td>
<td>0.71003</td>
<td>—</td>
<td>—</td>
<td>66.58</td>
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<tr>
<td>6(b)</td>
<td>12.0051 × 10^{-9}</td>
<td>—</td>
<td>0.31039</td>
<td>—</td>
<td>—</td>
<td>66.47</td>
</tr>
</tbody>
</table>

*Figure 8. Overall best-fit $D_s$ correlation for the three metal ions on bone char.*
The derived values of the non-dimensional adsorption energy range, \( \alpha \), for the individual metals are comparable (3.58–4.51) and close to those derived for dyes on carbon and zeolite, \(^{38}\) little further inference should be attempted in the absence of more detailed studies examining the temperature dependence of \( D_s \).

**ACKNOWLEDGEMENTS**

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The software used in this research may be downloaded from the HKUST institutional repository.

**REFERENCES**

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