

## Equilibrium studies for the sorption of metal ions onto Chitosan

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The sorption of four metal ions, viz. Hg(II), Cu(II), Ni(II) and Zn(II) onto chitosan has been studied. The monolayer sorption capacity is 815, 222, 164 and 75 mg g<sup>-1</sup> chitosan for mercury, copper, zinc and nickel ions respectively, at 25°C and at a particle size in the range of 710-1000 µm. The effect of chitosan particle size and solution temperature on the sorption capacity has been investigated. The equilibrium isotherms have been analysed using the Langmuir isotherm model.

The removal of pollutants from aqueous effluents by sorption onto solids produces high quality treated waste water. Many sorbent materials have been tested<sup>1-3</sup> for various pollutants. Chitosan, derived from prawn shell waste, shows specific sorption properties. Chitosan has been put to many uses as an adsorbent<sup>4</sup>. The sorption of metals onto peat moss<sup>8</sup>, carbon<sup>9</sup>, and chitin<sup>10</sup>, peanut husk and aged bark<sup>11</sup>, polyamine-carbohydrates<sup>12</sup>, softwood sawdust<sup>11</sup> and straw<sup>13</sup>, substituted poly-anhydroglucosides<sup>14</sup>, cellulose derivatives<sup>15</sup> has been studied.

However, chitosan derived from a natural polysaccharide contains a higher nitrogen content (7.2%) and is much superior as a metal adsorbent<sup>16-18</sup>. Hauer<sup>19</sup> compared the chelating abilities of chitosan with the commercially available chelating polymers, viz. Chelex 100 resin and Amberlite XE-318 resin.

The fact that chitosan is relatively inert to alkali metals and alkaline earth metals makes it superior to the other polymers tested for transition metal recovery in alkaline or saline waters. Elution of metals from chitosan columns may be achieved by a dilute solution of sulphuric acid and ammonia sulphate<sup>20</sup>.

This paper presents the results of a series of equilibrium isotherm studies for the sorption of mercury (2<sup>+</sup>), copper (2<sup>+</sup>), nickel (2<sup>+</sup>) and zinc (2<sup>+</sup>) ions onto chitosan. The effects of solution temperature and chitosan particle size have been investigated.

### Materials and Methods

Chitosan was obtained as follows. The prawn shells were deproteinated using sodium hydroxide, followed by calcium carbonate removal with hydrochloric acid. After washing, drying, crushing and sieving, the product obtained at this stage was

chitin. This chitin was deacetylated to chitosan by refluxing at 110°C with sodium hydroxide.

Solutions of metal ions were obtained by dissolving analar grade salts, namely, copper sulphate, mercuric chloride, zinc sulphate and nickel sulphate in water. The stock solutions were diluted as required.

### Equilibrium isotherms

These were determined by thoroughly shaking a suspension of chitosan (0.1 g) with metal solution (0.050 ml) in a sealed jar at constant temperature. Initial concentrations of metal ranged from 5 ppm to 1000 ppm for all systems. Equilibrium isotherms were determined for two variables: (i) variation of adsorbent (chitosan) particle size, ranging from 210-1000 µm in diameter, at 25°C; and (ii) variation of temperature of the metal solution, at a constant particle size of adsorbent, i.e. at 25° or 30°, 40° and 60°.

The system containing chitosan and metal solution (zinc as nickel) was kept for sufficient time interval (7 to 14 days) to allow for equilibrium to be established, after which the samples were filtered, and the concentration of the metal solution determined by atomic absorption spectrophotometry. The results were treated as follows:

$C_0$  = initial metal concentration (ppm)

$C_e$  = metal concentration left in solution at equilibrium (ppm)

$\frac{X}{M} = \frac{C_0 - C_e}{20 \times 0.1}$  = amount of metal taken up per gram of chitosan (mg/g)

$X/M$  (mg/g) was plotted against  $C_e$  (ppm) to produce an equilibrium adsorption isotherm for each variable.

### Results and Discussion

Figure 1 shows the equilibrium capacity ( $X/M$   $\text{mg g}^{-1}$ ) of chitosan, for the adsorbent particle size in the range of 710-1000  $\mu\text{m}$  for mercury, copper, nickel and zinc, at 25°C. The capacity of chitosan for each metal is 815, 222, 164 and 75  $\text{mg g}^{-1}$  for the sorption of mercury, copper, zinc and nickel ions, respectively.

Muzzarelli<sup>21</sup> gave the order of collection rates of metal onto chitosan as:  $\text{Cu} > \text{Ni} > \text{Zn}$ ; this order is the same order as the Irving-Williams series<sup>22</sup> for the collection rates for the first-row transition metals. The discrepancy in the results may be due to the fact that Muzzarelli measured the 'rate' of uptake as opposed to the 'saturation capacities' as in this work, and furthermore his investigations were made at very low initial concentrations of metals.

Equilibrium isotherms were constructed for each metal solution in contact with chitosan; for variation of temperature of solution and at differ-

ent particle sizes of adsorbent. Table 1 records the saturation capacity of each metal, at various particle sizes ( $\text{mg g}^{-1}$ ) and Figs 2 and 3 show the equilibrium isotherms at various particle sizes for each

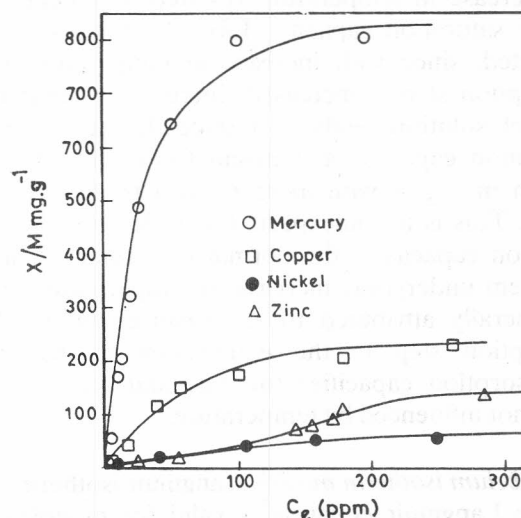


Fig. 1—Equilibrium capacity for each metal

Table 1—Langmuir constants for each metal ion on Chitosan

| Langmuir constants |                                 |                             |                                       |                                  |                                         |                        |
|--------------------|---------------------------------|-----------------------------|---------------------------------------|----------------------------------|-----------------------------------------|------------------------|
| Metal              | Particle size ( $\mu\text{m}$ ) | Temp ( $^{\circ}\text{C}$ ) | $Q_0$ $\text{mg} \cdot \text{g}^{-1}$ | $b$ $\text{mg}^{-1} \text{dm}^3$ | $K_L$ $\text{dm}^3 \cdot \text{g}^{-1}$ | Range applicable (ppm) |
| Copper             | 710-1000                        | 25                          | 222.0                                 | 0.024                            | 5.3                                     | 0-300                  |
|                    | 500-710                         | 25                          | 220.0                                 | 0.030                            | 6.6                                     | 0-300                  |
|                    | 355-500                         | 25                          | 213.0                                 | 0.036                            | 7.7                                     | 0-300                  |
|                    | 210-355                         | 25                          | 189.0                                 | 0.041                            | 7.7                                     | 0-300                  |
|                    | 710-1000                        | 40                          | 220.0                                 | 0.025                            | 5.5                                     | 0-300                  |
|                    | 710-1000                        | 60                          | 126.0                                 | 0.028                            | 3.5                                     | 0-300                  |
| Mercury            | 710-1000                        | 25                          | 815.0                                 | 0.041                            | 33.4                                    | 0-600                  |
|                    | 500-710                         | 25                          | 734.0                                 | 0.045                            | 33.0                                    | 0-600                  |
|                    | 355-500                         | 25                          | 727.0                                 | 0.046                            | 33.4                                    | 0-1000                 |
|                    | 210-355                         | 25                          | 718.0                                 | 0.046                            | 33.0                                    | 0-1000                 |
|                    | 500-710                         | 40                          | 555.0                                 | 0.045                            | 24.9                                    | 0-600                  |
|                    | 500-710                         | 60                          | 543.0                                 | 0.036                            | 19.5                                    | 0-1000                 |
| Nickel             | 710-1000                        | 25                          | 75.0                                  | 0.009                            | 0.71                                    | 0-200                  |
|                    | 500-710                         | 25                          | 62.0                                  | 0.013                            | 0.81                                    | 0-300                  |
|                    | 355-500                         | 25                          | 71.4                                  | 0.010                            | 0.71                                    | 0-250                  |
|                    | 210-355                         | 25                          | 66.0                                  | 0.018                            | 1.19                                    | 0-300                  |
|                    | 500-710                         | 40                          | 62.5                                  | 0.020                            | 1.25                                    | —                      |
|                    | 500-710                         | 60                          | 56.0                                  | 0.029                            | 1.62                                    | —                      |
| Zinc               | 710-1000                        | 25                          | 164.0                                 | 0.007                            | 1.21                                    | —                      |
|                    | 500-710                         | 25                          | 120.0                                 | 0.010                            | 1.20                                    | 10-400                 |
|                    | 355-500                         | 25                          | 113.0                                 | 0.010                            | 1.13                                    | —                      |
|                    | 210-355                         | 25                          | 98.0                                  | 0.013                            | 1.27                                    | —                      |
|                    | 500-710                         | 40                          | 125.0                                 | 0.010                            | 1.25                                    | —                      |
|                    | 500-710                         | 60                          | 102.0                                 | 0.013                            | 1.33                                    | —                      |

\* $Q_0$  = saturation capacity

metal. The influence of particle size does not greatly influence the capacity of metal sorption.

The effect of temperature on the saturation capacity was not very significant. In all metal systems an increase in temperature resulted in a decrease in the saturation capacity (Table 1). This is to be expected, since with increase in temperature the desorption step is increased. Increase in temperature of solution tends to reduce the equilibrium saturation capacity of chitosan for each metal as shown in Fig. 4 with mercury as a representative metal. This is not unexpected as a decrease in adsorption capacity is the normal behaviour of such a system undergoing increase in temperature. This is generally attributed to an enhancement of the desorption step in the equilibrium mechanism. The sorption capacities for zinc and nickel ions were not influenced by temperature.

#### Equilibrium isotherm models: Langmuir isotherm

The Langmuir equation is valid for monolayer sorption on a surface containing a finite member of sites. The model assumes uniform energies of sorption on the surface and no transmigration of

sorbate in the plane of the surface. The Langmuir expression was represented in this work by Eq. (1):

$$\frac{X}{M} = \frac{K_L \cdot C_e}{1 + b \cdot C_e} \quad \dots (1)$$

where  $K_L = Qb$ .

Equation (1) may be arranged in the linear form (2)

$$\frac{C_e}{X/M} = \frac{1}{K_L} + \frac{b \cdot C_e}{K_L} \quad \dots (2)$$

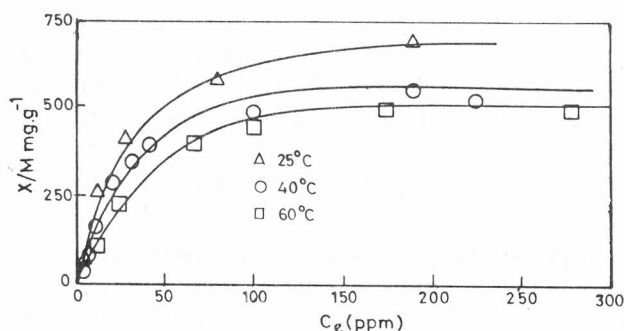


Fig. 4—Equilibrium isotherm for mercury sorption onto chitosan—variation of temperature ( $dp = 710\text{--}1000\ \mu\text{m}$ )

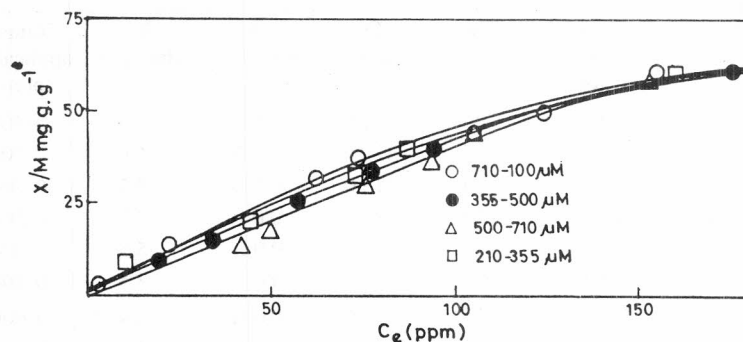


Fig. 2—Equilibrium isotherm for nickel sorption onto chitosan of  $dp$  ( $T = 25^\circ\text{C}$ )

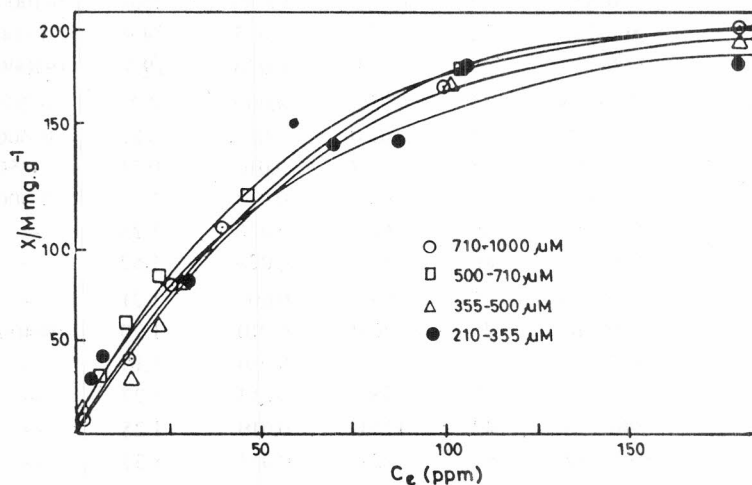


Fig. 3—Equilibrium isotherm for copper sorption onto chitosan—variation of  $dp$  ( $T = 25^\circ\text{C}$ )

Hence a plot of  $C_e/X/M$  versus  $C_e$  is linear with intercept  $^{-1} = K_L$  and the slope =  $b$ . Particle size and temperature effects on the Langmuir plots for selected metals are represented in Fig. 5.

The  $K_L$  and  $b$  values derived from the linear Langmuir plots are given in Table 1. In general with variation of particle size and temperature within each metal group the  $K_L$  and  $b$  values do not differ greatly,  $K_L$  and  $b$  values only differ by an order of magnitude. Although the difference in  $K_L$  and  $b$  values are only slight, overall a trend is established in that as the particle size increases, both  $K_L$  and  $b$  values decrease. However as previously stated the trend is not greatly significant. In the cases of zinc and nickel, the opposite

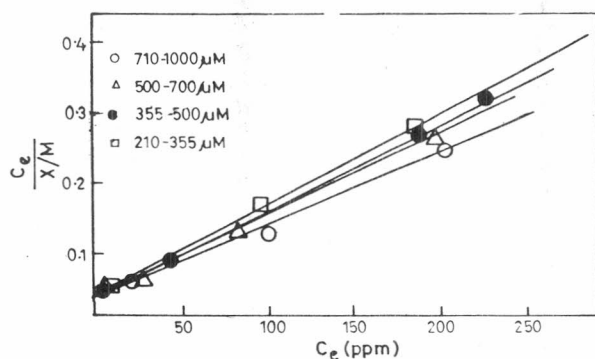


Fig. 5A—Langmuir plot of mercury sorption onto chitosan-variation of  $d_p$  ( $T=25^\circ\text{C}$ )

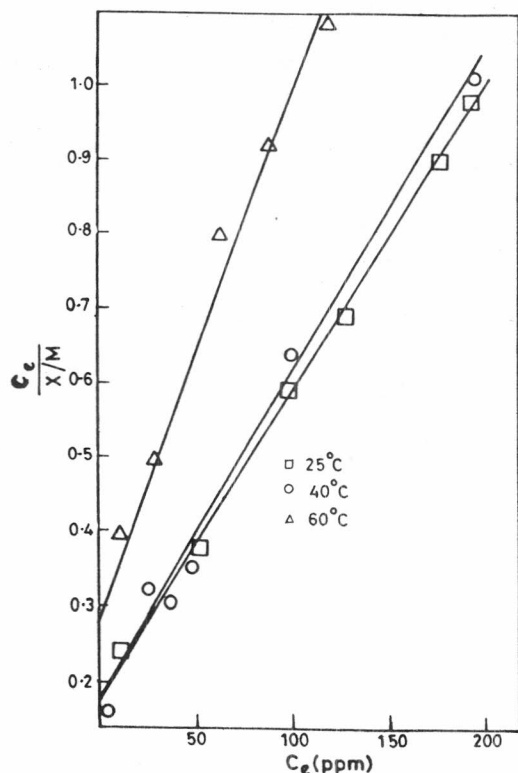


Fig. 5B—Langmuir plot of copper sorption onto chitosan-variation of temperature ( $d_p = 710-1000 \mu\text{m}$ )

situation arises in that as the temperature increases, and also when  $d_p$  decreases the constant  $b$  increases. The constant  $b$  in the Langmuir equation is related to the energy or net enthalpy of sorption. The constant,  $K_L$ , can be used to determine the enthalpy of adsorption, using the Clausius-Clapeyron equation (3)

$$K_L = A_c \exp \left( -\frac{\Delta H}{R.T.} \right) \quad \dots (3)$$

Hence a plot of  $\log K_L$  versus  $1/T(K)$  as shown in Fig. 6

yields a gradient;  $-\frac{\Delta H}{2.303 R}$  from which  $-\Delta H$  may be

calculated.  $\Delta H$  for mercury, copper, zinc and nickel were determined as:  $+13.4$ ,  $+8.2$ ,  $-17.7$  and  $-2.5 \text{ kJ mol}^{-1}$  respectively. The  $\Delta H$  value for mercury suggests that the mercury-chitosan reaction is slightly more favourable than the copper-chitosan reaction. The values for the nickel and zinc suggest an exothermically enhanced reaction, as opposed to an exothermic reaction for mercury and copper.

The enthalpy values for the adsorption of nickel and zinc ions represent endothermic adsorption reflecting that the trend for adsorption is not highly favourable. The same trend is reflected in the values of the equilibrium constants for nickel and zinc ions:  $K_L$  values being much lower than those for copper and mercury. This implies that the rate constant for desorption is relatively higher for nickel and zinc and therefore adsorption is not as favourable and the adsorption capacities are not as high.

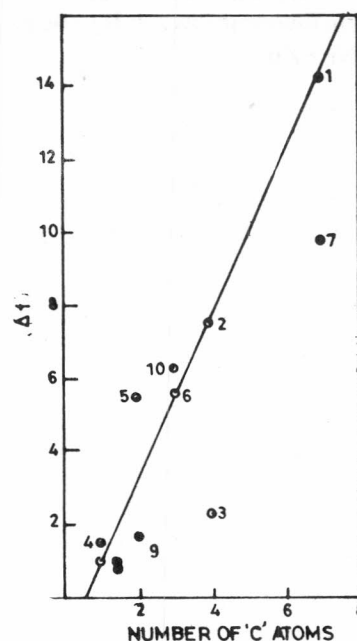


Fig. 6—Variation of Langmuir equilibrium constant with temperature for sorption of metals on chitosan

Table 2—Separation factor (a) values for different metals at different particle sizes on temperature

| Metal<br>(220 ppm) | 855 $\mu\text{m}$ | 505 $\mu\text{m}$ | 427 $\mu\text{m}$ | 282 $\mu\text{m}$ | 40°C | 60°C |
|--------------------|-------------------|-------------------|-------------------|-------------------|------|------|
| Copper             | 0.17              | 0.14              | 0.12              | 0.11              | 0.15 |      |
| Mercury            | 0.11              | 0.10              | 0.10              | 0.10              | 0.10 | 0.12 |
| Nickel             | 0.36              | 0.28              | 0.33              | 0.22              | 0.20 | 0.15 |
| Zinc               | 0.42              | 0.33              | 0.33              | 0.28              | 0.33 | 0.28 |

### Isotherm shape

The shape of an isotherm can indicate the favourability of adsorption of solute by the adsorbent. Weber and Chakravorti<sup>23</sup> and Hall *et al.*<sup>24</sup> proposed a system of establishing the favourability of an isotherm by noting that the essential characteristic of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter 'a' which is defined by Eq. (4):

$$a = \frac{1}{1 + b \cdot C_0} \quad \dots (4)$$

The parameter indicates the shape of the isotherm as follows:

| Values of 'a' | Type of isotherm |
|---------------|------------------|
| $a > 1$       | Unfavourable     |
| $a = 1$       | Linear           |
| $0 < a < 1$   | Favourable       |
| $a = 0$       | Irreversible     |

Referring to Table 2, it is obvious that chitosan is a good sorbent for all the metals. According to this classification system favourability tends to be in the order of  $\text{Hg} > \text{Cu} > \text{Ni} > \text{Zn}$ .

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