



## Adsorption of heavy metals in slow sand filters

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CHEMICAL CONTAMINANTS AT low concentrations are difficult to remove from water. Chemical precipitation, reverse osmosis and other methods become inefficient when contaminants are present in trace concentrations. The process of adsorption is one of the few alternatives available for such situations (Huang and Morehart, 1991). A number of adsorbent materials have been studied for their capacity to remove heavy metals, including activated carbon, activated alumina, ion exchange resins, crushed coals etc. Some of these materials, such as ion exchange resins are totally effective but expensive and others, such as coal and straw, are inexpensive but ineffective. Activated carbon is very effective in removing heavy metals, but is readily soluble under extreme pH conditions (Huang and Blankenship, 1989). Peat moss has been found as very effective in adsorbing heavy metals (Ho, 1995). In the present study Slow Sand Filters (SSFs) are tried to remove heavy metals and found very effective (Muhammad *et al*, 1997). Experimental results on the influences of process variables in removing heavy metals by SSFs demonstrated that adsorption was one of the mechanisms of the removal of heavy metals (Muhammad *et al*, 1997). To confirm this prediction/hypothesis, batch adsorption tests were carried out. This paper deals with the results of the batch adsorption tests to establish adsorption isotherms and adsorption capacity of the sand for the selected heavy metals.

### Adsorption Isotherms

Two important physiochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibria of the adsorption and the kinetics. Equilibrium studies give the capacity of the adsorbent (Ho, 1995). The equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. There are two types of adsorption isotherms: Langmuir adsorption isotherms and Freundlich adsorption isotherms.

#### Langmuir isotherm

Irving Langmuir, an American chemist who was awarded the Nobel prize for chemistry in 1932 for "his discoveries and researches in the realm of surface chemistry", developed a relationship between the amount of gas adsorbed on surface and the pressure of that gas. Such equations are now referred to as Langmuir adsorption isotherms, a theoretical adsorption isotherms in the ideal case. The Langmuir

adsorption isotherm is often used for adsorption of a solute from a liquid solution. The Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption and is often expressed as:

$$Q_e = X_m K C_e / (1 + K C_e) \quad (\text{Casey, 1997})$$

where:

$Q_e$  is the adsorption density at the equilibrium solute concentration  $C_e$  (mg of adsorbate per g of adsorbent)

$C_e$  is the concentration of adsorbate in solution (mg/l)

$X_m$  is the maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per g of adsorbent)

$K$  is the Langmuir constant related to energy of adsorption (l of adsorbent per mg of adsorbate)

The above equation can be rearranged to the following linear form:

$$C_e / Q_e = 1 / X_m K + C_e / X_m$$

The linear form can be used for linearisation of experimental data by plotting  $C_e / Q_e$  against  $C_e$ . The Langmuir constants  $X_m$  and  $K$  can be evaluated from the slope and intercept of linear equation.

#### Freundlich isotherm

Herbert Max Finley Freundlich, a German physical chemist, presented an empirical adsorption isotherm for non-ideal systems in 1906. The Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as:

$$Q_e = K_f C_e^{1/n} \quad (\text{Casey, 1997})$$

where:

$Q_e$  is the adsorption density (mg of adsorbate per g of adsorbent)

$C_e$  is the concentration of adsorbate in solution (mg/l)

$K_f$  and  $n$  are the empirical constants dependent on several environmental factors and  $n$  is greater than one.

This equation is conveniently used in the linear form by taking the logarithmic of both sides as:

$$\ln Q_e = \ln K_f + 1/n \ln C_e$$

A plot of  $\ln Q_e$  against  $\ln C_e$  yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constants can be determined from the slope and the intercept.

### Method used for Batch Adsorption Tests

The method developed by Ho in 1995 was used for the batch adsorption tests for different heavy metals. The procedures for the tests are as follows:

- 1g of sand as an adsorbent was taken in 250 mls of metal solution. The concentration of the adsorbent was 4 g/l.
- the conical flasks were capped and shaken in the flask shaker at 200rpm for 4 hours.
- the temperature was fixed at 20°C and pH was adjusted at 7.2 to 7.5.
- at least five different concentrations of each metal were considered.
- the sample was filtered through Whatman 540 mm filter paper and the effluent concentration determined.
- $Q_e$  was determined and  $C_e$  vs  $C_e/Q_e$  and  $\ln C_e$  vs  $\ln Q_e$  were plotted.

### Results and discussions

To establish the adsorption isotherms and evaluate the adsorption capacity of sand, individual metal was tested in triplicate. The results described here are the average of three sets of tests.

#### Batch adsorption test results for Cu, Cr, Pb and Cd

Tables 1, 2, 3, and 4 describe summaries of the batch adsorption test results to establish Langmuir and Freundlich isotherms.

The values of  $C_e$  was plotted against the values of  $C_e/Q_e$ , yielding straight line relationships for each of Cu, Cr, Pb

and Cd. Similarly the values of  $\ln C_e$  were plotted against the values of  $\ln Q_e$ , also giving straight lines for all four heavy metals. The linear equations and the correlation coefficients are summarised in Table 5. These results (and the fact that the regression coefficients were very close to one, indicating good linearity) confirm that the adsorption of Cu, Cr, Pb and Cd on sand follow the two theories of adsorption - the Langmuir and the Freundlich adsorption isotherm (respectively).

The Langmuir constant  $X_m$  (maximum adsorption capacity) and the Freundlich constant  $K_f$  were obtained from the linear equations. The values are summarised in Table 6.

The maximum adsorption capacity of sand is the highest for Pb followed by Cu, Cr and Cd. The Freundlich constant  $K_f$  for Cu is greater than the other heavy metals. It may be due to the higher influent concentration of Cu. The values of  $n$  for all four heavy metals were obtained as greater than one which indicates good adsorption of these metals onto sand.

### Conclusions

- The results build on earlier work (Muhammad *et al*, 1997) in showing that slow sand filters are effective in the removal of heavy metals. This has particular significance to developing countries as SSFs are probably the most appropriate water treatment option in such circumstances. In addition, many developing countries suffer from chemical contamination of water supplies, largely due to uncontrolled industrial activity - and so

**Table 1. Summary of the batch adsorption test results for Cu**

No of observations	$C_e$ (mg/l)	$Q_e$ (mg/g of sand)	$C_e/Q_e$	$\ln C_e$	$\ln Q_e$
1	940	145.0	6.48	6.84	4.98
2	1860	250.0	7.44	7.52	5.52
3	2750	312.5	8.80	7.92	5.74
4	3200	332.5	9.62	8.08	5.80

**Table 2. Summary of the batch adsorption test results for Cr**

No of observations	$C_e$ (mg/l)	$Q_e$ (mg/g of sand)	$C_e/Q_e$	$\ln C_e$	$\ln Q_e$
1	128.0	28.9	4.43	4.85	3.36
2	268.5	55.8	4.82	5.60	4.02
3	404.6	79.9	5.06	6.00	4.38
4	560.0	108.6	5.60	6.32	4.69

**Table 3. Summary of the batch adsorption test results for Pb**

No of observations	$C_e$ (mg/l)	$Q_e$ (mg/g of sand)	$C_e/Q_e$	$\ln C_e$	$\ln Q_e$
1	68.0	15.0	4.54	4.22	2.71
2	96.0	20.5	4.70	4.56	3.02
3	260.0	54.0	4.80	5.56	3.99
4	355.0	71.5	4.96	5.87	4.27

**Table 4. Summary of the batch adsorption test results for Cd**

No of observations	$C_e$ (mg/l)	$Q_e$ (mg/g of sand)	$C_e/Q_e$	$\ln C_e$	$\ln Q_e$
1	115.8	14.3	8.1	4.75	2.66
2	256.3	29.3	8.8	5.55	3.38
3	412.9	40.4	10.2	6.02	3.70
4	543.6	49.2	11.1	6.30	3.90

**Table 5. Linear regression data for Langmuir and Freundlich isotherms**

Heavy metal	Langmuir data		Freundlich data	
	linear equation	correlation coefficient $r^2$	linear equation	correlation coefficient $r^2$
Cu	$y=0.0011x+5.390$	0.9916	$y=0.6709x+0.418$	0.9867
Cr	$y=0.0018x+4.275$	0.9439	$y=0.901x-1.0163$	0.9996
Pb	$y=0.0012x+4.5108$	0.9022	$y=0.9521x-1.3128$	0.9999
Cd	$y=0.0072x+7.1472$	0.9893	$y=0.7937x-1.0759$	0.9957

(note: for Langmuir data  $x=C_e$  and  $y=C_e/Q_e$ ; for Freundlich data  $x=\ln C_e$  and  $y=\ln Q_e$ )

**Table 6. Comparison of the isotherm constants**

Heavy metal	Langmuir Constant $X_m$ (Maximum adsorption capacity in mg/g of sand)	Freundlich Constant $K_f$
Cu	719.0	1.52
Cr	556.0	0.36
Pb	833.0	0.27
Cd	139.0	0.34

a water treatment technique which is able to deal with such pollutants in an effective way is very valuable.

- Adsorption of Cu, Cr, Pb and Cd onto sand satisfied the Langmuir and Freundlich isotherms.
- The adsorption capacity of sand was the highest for Pb followed by Cu, Cr and Cd.
- The values of Freundlich exponent  $n$  were greater than one for all four heavy metals confirming the adsorption of these metals onto sand.
- Hence the hypothesis of adsorption of heavy metals in slow sand filters as a significant mechanism of removal is confirmed by the batch adsorption test results. Traditionally, much of the treatment capacity of SSFs has been attributed to the action of the microbiological schmutzdecke layer. This research shows that the adsorption activity of the sand bed is also significant.

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