A Study on the Effects of Dosage Variation of Sawdust as an Absorbent on Uptake Kinetics of Hexavalent Chromium in Aqueous Solutions

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Introduction

Sawdust as the most expensive and the most abundant adsorbent has the capacity of adsorbing heavy metals in water and wastewater. Recently, some agricultural wastes such as fern leaves, sawdust, wheat bran, wood, corn and so on have widely been used to remove heavy metals from aqueous solutions. Sawdust is produced daily in industries related to wood processing. Several studies have done on the capability of sawdust to remove heavy metals from industrial wastewater. In this study, determination of equilibrium time and major parameters of adsorption isotherms on the basic equations are considered. On one hand, adsorption isotherms were achieved by changing the mass concentration but the temperature was considered constant. On the other hand, in both methods, equilibrium time was presumed stable, but the concentrations (adsorbent mass) were considered variable. Therefore, the main purpose of this study is to investigate the effects of changing mass balance of adsorbent on adsorption equilibrium time. Another objective of this study is to achieve a mathematical definition for the relationship between initial concentration and absorption efficiency.

Materials & Methods

Chromium ion storage solution (1000 mg/L) using Titrisol Cr6 was prepared with distilled water. Sawdust produced in local workshops with the particle size of 500 microns was gained.

The collected sawdust was thoroughly washed by detergents and oven-dried in 70 degrees of Celsius for 6 hours. Batch experiments for determination of pH, equilibrium time and the efficiency of various chromium concentrations absorption was conducted. As for the determination of kinetic parameters of the models, in this study chromium uptake was studied. The kinetic equations including Avrami, pseudo first-order, and pseudo-second order, are given in Table 1.

Table 1: Kinetic adsorption models

Kinetic model	Non-linear equation
Avrami	$q_t = q_e.\{1-\exp[-(k_{AV}.t)]^{n_{AV}}\}$
Pseudo-first order	$q_t = q_e.[1-\exp(-k_f.t)]$
Pseudo-second order	$q_t = \frac{k_s.q_e^2.t}{1+q_e.k_s.t}$ $h_0 = k_s.q_e^2$

This study investigated the kinetic and equilibrium models employing the non-linear fitting method, using facilities of the SPSS software (version 14.0). In addition, the models were also evaluated by an error function measuring the differences in the amount of dye up taken by the adsorbent predicted by the models and the actual q measured experimentally.

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$$F_{error} = \sqrt{\sum_{1}^{p} \left(\frac{q_{i\,model} - q_{i\,experimental}}{q_{i\,experimental}}\right)^2 . \left(\frac{1}{p-1}\right)} \quad (1)$$

Where $q_{i\ model}$ is each value of q predicted by the fitted model and $q_{i\ experimental}$ is each value of q measured experimentally, and p is the number of experiments performed.

Results and Discussion

Absorption values at pH 7 in a descending order are equal to SD_1 (52.74%), SD_{10} (67.03%), SD_{20} (71/53%) and SD_{50} (83.50%). The initial concentration in all solutions is 200 mg/ml.

Equilibrium times order will be $SD_{50} \prec SD_{20} \prec SD_{10} \prec SD_1$. As it can be seen, absorption equilibrium time decreases with the increase in adsorbent mass. Maximum equilibrium time for the balance of the adsorbents SD_1, SD_{10}, SD_{20} and SD_{50} are 110, 105, 100 and 80 minutes respectively. Initial concentrations are 31 / 5, 76/14, 05/15 and 77/19 mm g ml respectively. By increasing the concentrations of 5.31 (SD_1), 14.76 (SD_{10}), 15.05 (SD_{20}) and 19.77 (SD_{50}) to 200 mg L, equilibrium times of all absorbents are reduced.

So it can be defined as below:

Mcap: mass of adsorbent capacity (mass capacity, mg)

Mcon: mass of initial concentration (mass concentration mg)

Mce: equilibrium concentration

E: adsorption efficiency

$$E = \frac{M_{con} - M_{ce}}{M_{con}} = \frac{M_x}{M_{con}} \quad (2)$$

IF:

$$M_{con} \succ M_{cap} \quad \lim_{M_{con}\to\infty} \frac{M_{con} - M_{ce}}{M_{con}} = \lim_{M_{con}\to\infty} \frac{M_x}{M_{con}} \Rightarrow \lim_{M_{con}\to\infty} \frac{M_{cap}}{M_{con}} = 0 \quad (3)$$

$$M_{con} \leq M_{cap} \quad \lim_{M_{con}\to 0} \frac{M_{con} - M_{ce}}{M_{con}} = \lim_{M_{con}\to 0} \frac{M_x}{M_{con}} \Rightarrow \lim_{M_{con}\to 0} \frac{M_{con}}{M_{con}} = 1 \quad (4)$$

According to equation 3 considering mass concentration limits (when $M_{con} \to \infty$) it can be expressed that the adsorbent could absorb metal ion at a maximum level of its capacity which equals a constant quantity (the limit equals zero). In equation 4 when mass concentration is lower than mass capacity and M_{cap} approaches to zero, the adsorbent capability is limited to its mass concentration. In other words M_{cap} will be equal to M_{con}:.

One of the important studies of absorption process is absorption kinetics study. Through this method, uptake variations are shown with time. Avram fitted models, and Hu et al. and Lagergrn works on the data obtained from kinetic absorption experiments in terms of concentration of 1 mg/L Cr and the results of fitting kinetic models show aspects of all three models describing the absorption process well. But Avram model was of the lowest error factor (0.036) and the highest correlation coefficient (0.999%). So it is selected as the model best describing the kinetics of chromium absorbed by sawdust. The comparison of metal uptake capacity of chromium (Cr6 +) in other studies (Table 2) shows that the absorption capacity of sawdust as an absorbent is higher than the others.

Table 2: Comparison of maxima adsorption capacities for chromium taken-up

References	dosage absorbent (gL-1)	Initial metal concentration (mgL-1)	Optimum pH	Adsorption capacity (mgg-1)	Adsorbent
Lima ,et al.,2008	6	10	4	1.6	Active aluminum
Bishnoi ,et al., 2003	12	10	2	0.79	rice husk
Rao ,et al., 2002	12	50	6	0.03	bagasse
Chakir, et al., 2002	10	20	5	1.4	perlyte
Daneshvar and Salari , 2002	9.3	44	1	0.28	Aluminum Falzghal Sevilla
Present study	1	1	7	3.7	sawdust

Conclusions

Mathematical Relationship between mass absorption efficiency, absorbent solution and initial concentration showed that although increasing the sorbent's mass absorption will increase the efficiency, if the initial concentration of a certain amount (absorption mass capacity) approaches to zero, the efficiency of all absorbents will rise to 100%. This is also true about the concentrations approaching to infinity. The calibration results show that the regression coefficient of Avram model is 0.999 and its error factor is 0.036. The data gained from Lagergren and Ho et al. models described the absorption kinetics better.

Key words

Chromium, Sawdust, Equilibrium time, Kinetic models, Absorption efficiency