

Use of Wollastonite for Tailing Waste Management Enriched in Mn (II) and Zn (II)

A.K. Singh, S. Gupta, R.P. Singh and N.C. Karmakar

Department of Mining Engineering, Institute of Technology,
Banaras Hindu University, Varanasi-221005, India

ABSTRACT: This paper deals the study of use of wollastonite for the treatment of tailing wastes enriched in Mn(II) and Zn(II). The efficiency of wollastonite was tested at different concentrations and temperatures at suitable pH of the system. It was found that low concentration favors the uptake of adsorbate species. However effect of temperature varies with the nature of adsorbate Species The process of uptake follows a first order adsorption rate kinetics and obeys Langmuir model of adsorption isotherm. The removal process has also been found to be partially diffusion controlled and mass transfer co-efficient have been determined to explain the mechanism of adsorption. The effect of pH has been discussed incorporating various surface site reactions. A generalized empirical models is proposed for different initial concentrations and temperatures

1. INTRODUCTION

Rapid industrialization is posing problems, such as environmental pollution, which is threatening the very existence of living beings. The presence of heavy metals in the environment, released by polluting industries, is of major concern because of its toxicity and threat to the environment. Anthropogenic of heavy metals include wastes from the electroplating and metal finishing industries, metallurgical industry, chemical and battery manufacturing industries, mining and mineral processing industry, acid mine drainage and leachates from land filled by mine wastes.” (Singh et al, 2004 & 2006).

The present investigation is aimed to develop a suitable and economic method for the treatment of mine tailing wastes enriched in Mn(II) and Zn(II) prior to their discharge in the environment. An environment friendly adsorption technique employed in the present study is considered as an advanced method for water treatment due to its simplicity, ease in handling and economic viability (Qiming et al, 1999 and Inow et al. 2004).

Some conventional adsorbents have been utilized for the removal of heavy metals in past (Adams et al 2005, Melegy et al 2005 and Akar et al 2005). However many of these, such as

activated carbon, activated alumina and activated silica etc are very costly. Keeping the above facts the utility of wollastonite a clay mineral has been tested as unconventional adsorbent for the treatment of mine tailing waste enriched in Mn(II) and Zn(II).

2. MATERIAL AND METHODS

2.1 Physico Chemical Analysis of Adsorbent

Wollastonite was obtained from m/s Wolkem, Udaipur, Rajasthan. It was used as such after grinding and sieving through 53, 75 and 125 μm pore size sieves. All the chemicals used were of analytical reagent grade, and were obtained from B.D.H. Bombay. The average particle size was measured by HiAC 320, Model- 8002917 (Royco Instruments, Div. USA) and surface charge by laser zee meter, model- 500 (Peutem, Ine N.Y., USA) the surface area was measured by a triple point Nitrogen gas adsorption method using quantasorb surface area analyser, model Qs - 7 (Quantachrome corp. USA) and porosity by mercury porosimeter. The India standard method (1960) were applied to analyze the adsorbent chemically

2.2 Method

Batch adsorption experiments were run by shaking 1.0 g of adsorbent with 50ml. aqueous solution of laboratory prepared waste containing known concentration of $MnSO_4$ and $ZnCl_2$ solutions in different glass bottles kept in a temperature controlled shaking water bath with a constant speed of 125 rpm at the end of pre-selected time intervals the bottles were taken out from the shaker and reaction mixtures were centrifuged at 1500 rpm, The progress of adsorption was assessed by determining the concentration of adsorbate species e.g. Mn (II) and Zn(II) by spectrophotometric method using spectrophotometer and also confirmed some times atomic absorption spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Characterization of Adsorbent

The chemical analysis of wollastonite indicates the presence of mainly silica and calcium oxide and with trace amounts of other oxides in the form of impurities Table 1. It was thus expected that the adsorbate species will be removed mainly by SiO_2 and/or CaO . Infra red, x-ray diffraction and Scanning Electron Microscope (SEM) of wollastonite also support chemical and physical analysis results and prove its utility as an adsorbent for waste water treatments.

Table 1: Chemical and physical characterization of wollastonite

Constituents	% by Weight
SiO_2	48.42
Al_2O_3	0.24
Fe_2O_3	0.26
CaO	48.48
Loss an ignition	2.50
Menu Particle diameter (m)	48×10^{-4}
Surface area ($m^2 g^{-1}$)	1.18
Porosity (Ep)	0.23
Density (P_p) ($g cm^{-3}$)	2.60
P^H_{zpc}	2.60

3.2 Effect of Contact Time and Adsorbate Concentration

It has been found that the removal of Mn(II) and Zn(II) increases with the lapse of time and attains equilibrium in 100 and 130 min. respectively by wollastonite. It is inferred from Table 2 that the percentage removal of aforesaid pollutants decreases with increase of initial concentrations. The maximum removal at low concentration is due to the fact that parking space at the surface of adsorbent is constant for all the initial adsorbent concentration while the number of adsorbing species are less in low initial concentration range in comparison to higher concentration range. The following correlations have been developed between percentage removal and initial adsorbate concentration (C_0) to predict successfully, the percentage removal of various pollutants by wollastonite at any initial concentration .

Table 2: Experimental and Model values for Mn (II) and Zn (II) removal by wollastonite at different initial concentrations

Adsorbate Specie	Concn.mg/l	Experm. Values	Model Values	% error
Mn(II)	10	80.00	81.24	1.55
	20	65.00	63.30	2.62
	30	53.33	54.70	2.57
Zn(II)	10	62.00	62.13	0.21
	15	53.33	51.55	3.34
	20	45.00	45.16	0.36

For Mn (II) - Wollastonite,

$$\% \text{ removal} = 186.11 C_0^{-0.32} \quad \dots(1)$$

for Zn (II) - Wollastonite ,

$$\% \text{ removal} = 179.17 C_0^{-0.46} \quad \dots(2)$$

The experimental and model values (calculated by above relationships) of percentage removal of different initial concentrations are recorded in Table 2 along with percentage error. Table 2 depicts that the model values are in good agreement with those of experimental showing

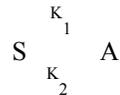
the validity of the above model. These results will be helpful during the fabrication of a treatment plant for the treatment of tailing wastes enriched in Mn(II) and Zn(II).

4. ADSORPTION DYNAMICS

The dynamics or adsorption is studied by considering the following steps:

4.1 Study of Rate Constant

The adsorption of Mn (II) and Zn(II) from liquid phase to solid phase can be considered as reversible reaction (Yadav et al., 1991) with an equilibrium being established between two phases. A simple first order reversible reaction kinetic model was therefore used to establish the rates or reaction which can be expressed as:



the rate equation for the above reaction may be expressed as:

$$\ln [1-u(t)] = K't \quad \dots(3)$$

Where K' is overall rate constant and $u(t) = q/q_e$ is the fractional attainment of equilibrium. Further

$$K_c = \frac{C_{se}}{C_{ae}} = \frac{K_1}{K_2} \quad \dots(4)$$

$$K' = K_1 + K_2 \quad \dots(5)$$

In which C_{Ae} (mg l^{-1}) and C_{Se} (mg l^{-1}) are the equilibrium concentration of Mn (II) and Zn(II) on the adsorbent and solution respectively, q and q_e both in (mg g^{-1}) are the amount of adsorbate at time t and at equilibrium respectively, K_1 and K_2 are the rate constants of adsorption and desorption respectively, and K_c is the equilibrium constant. The straight line plot of $\ln(1-u(t))$ vs t prove the validity of this kinetic model. The values of K' , K_1 and K_2 were calculated from the slopes of the respective plots and given in Table 3.

Table 3: Kinetic parameters for the Removal of Mn (II) and Zn (II) by adsorption on wollastonite

Adsorbate	$K \times 10^3$	$K_1 \times 10^3$	$K_2 \times 10^3$	K_d	$\beta_1 \times 10^5$
Mn (II)	38	30	1.60	0.020	1.78
Zn (II)	27	17	10.3	0.016	1.33

Units of K' , K_1 & K_2 are (min^{-1})
Units of K_d are ($\text{mg.g}^{-1} \cdot \text{min}^{0.5}$)
Units of β_1 are ($\text{cm} \cdot \text{Sec}^{-1}$)

4.2 Intra Particle Diffusion Study

Due to porous nature of the adsorbent pore diffusion is also expected in addition to surface adsorption. This possibility was tested in terms of a graphical relationship between amount of adsorbate vs Square root of time (Singh et al, 2004 & 2006)The dual nature of these plots may explained on the basic of the fact that the initial curved portion are due to surface adsorption while the linear portions are due to intra-particle diffusion effect. The rate constant of intra-particle diffusion k_{id} was calculated from the slopes of linear portion of respective plots and values are presented in Table 3.

4.3 Mass Transfer Coefficient Study

The mass transfer analysis for the adsorption of these pollutants species follows three consecutive steps: First adsorbates migrates from solution to the exterior surface of the adsorbent particles (surface adsorption). Secondly, the adsorbate species move into the pores of adsorbent particles and lastly they are adsorbed at sites on interior surface of the adsorbent particles. By the above facts McKay and co-workers have proposed a model for mass transfer study, (Singh et al, 2004 & 2006).

$$\ln\left(\frac{C_t}{C_0} - \frac{1}{1+mk}\right) = \ln\left(\frac{mk}{1+mk} - \frac{1+mk}{mk}\right)\beta_1 S_s t \quad \dots(6)$$

$$m = w/v, S_s = 6 m/d_p p_p (1-E_p)$$

Where, C_0 (mg l^{-1}) is the initial adsorbate concentration, C_t (mg l^{-1}) the adsorbate concentration at time t (min), m is the mass of adsorbent particle per unit volume of particle free slurry (g l^{-1}), k is the Langmuir constant $Q_0 \times b$ (l g^{-1}), β_1 is the mass transfer coefficient (cm s^{-1}), and S_s is the outer surface of adsorbent particle per unit volume of particle free slurry (cm^{-1}). A straight line plot of $\ln (C_0/C_t - 1/1+mk)$ Vs t shows the applicability of the above model for the system studied. The values of β_1 were determined by slopes and intercepts of the respective plots and given in table 3.

4.4 Adsorption Isotherm

The equilibrium data for the removal of Mn(II) and Zn(II) from effluents by wollastonite at 30°C temperature were analyzed in the light of a rearranged langmuir isotherm model.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad \dots(7)$$

Where c_e (mg l^{-1}) and q_e (mg g^{-1}) are the concentration and adsorbed amount of adsorbate species at equilibrium respectively. Q_0 and b are the langmuir constants related to the capacity and energy of the adsorption respectively. The linear plot of c_e/q_e Vs c_e suggest the applicability of the above model for the system studied, showing formation of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The values of Q_0 and b . were determined from the slopes and intercepts of linear plots and given in Table 4. The validity of the above model was further tested by regression analysis of the equilibrium data and given below:

For Mn (II) – wollastonite system

$$C_e/q_e = 1.0878 + 3.1448 C_e \quad \dots(8)$$

For Zn (II) – wollastonite system

$$C_e/q_e = 1.7013 C_e + 5.8242 \quad \dots(9)$$

Table 4: Langmuir parameters for the removal of Mn (II) and Zn (II) by wollastonite form aqueous solution at 30°C temperature

Adsorbate Specie	Graphical Values		Regression Values	
	$Q_0(\text{mg g}^{-1})$	$b(\text{l mg}^{-1})$	$Q_0(\text{mg g}^{-1})$	$b(\text{l mg}^{-1})$
Mn (II)	0.92	0.34	0.92	0.35
Zn (II)	0.58	0.30	0.59	0.29

5. EFFECT OF TEMPERATURE

It is evident from the results that removal of Mn(II) by wollastonite is exothermic in nature whereas removal of Zn(II) by wollastonite is endothermic in nature. In exothermic case the decrease in the extent of adsorption with rise of temperature is due to increase in escaping tendency of adsorbate species from the surface of adsorbent. However in case of endothermic adsorption process, the extent of removal increases with rise of temperature is mainly to an increase in the number of adsorption sites caused by the breaking of some internal bonds near the edge of the crystal (Yadav et al, 1991) An attempt has been made to correlate the percentage removal with the temperature and following correlations are obtained.

For Mn (II) – wollastonite system

$$\% \text{ removal} = 1.31 \times 10^7 T^{-6.14} \quad \dots(10)$$

For Zn (II) – wollastonite system,

$$\% \text{ removal} = 12.41 \times 10^{-8} T^{3.50} \quad \dots(11)$$

6. EFFECT OF pH

It is observed that the maximum removal of Mn (II) and Zn(II) by wollastonite is in basic pH range. The percentage removal is correlated with the pH of the solution and following correlations are obtained.

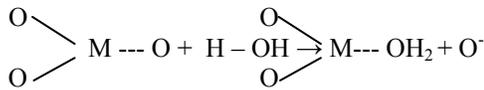
For Mn (II) – wollastonite system

$$\% \text{ removal} = 6.08 \text{ pH}^{1.17} \quad \dots(13)$$

For Zn (II) – Wollastonite system

$$\% \text{ removal} = 3.26 \text{ pH}^{1.37} \quad \dots(13)$$

The results obtained at various pH values have been explained on the basis of aqua-complex formation and its subsequent acid, base dissociation at the solid solution interface.



Where M stand for Si and Ca etc. It is often suggested that the adsorption of metal ions at the solid solution interface is not governed by the free metal concentration but the much stronger adsorbed hydroxo, sulfato, carbonato and other metal species (2).



The pH_{zpc} of wollastonite is 2.6 where as the pH_{zpc} of the major constituents silica is 2.2. The surface of adsorbent behaves positively charged below pH_{zpc} and negatively charged above pH_{zpc} . Hence the pH_{max} of adsorbate species is dependent on both, the surface change of adsorbent and presence of adsorbate species at that pH. Similar findings were also reported by several workers in the case of cation adsorption in past (Singh et al, 2004 & 2006).

7. CONCLUSION

This study indicate that wollastonite may be used as an efficient adsorbent for the treatment of Mn(II) and Zn(II) bearing waste streams. Wollastonite has a good adsorption capacity for Mn(II) and significant for Zn(II). The fitness of Langmuir's model in the present system. indicates the formation of monolayer coverage of the adsorbate species at the outer surface of adsorbent. The data thus obtained may prove of vital use for designing and fabricating a treatment

plant for tailing waste management enriched in manganese and zinc.

REFERENCES

- [1] Singh, A.K., Singh, S. and Halsan, S.H., 'Treatment of mine effluents contaminated with metal using Environmentally friendly Adsorption Techniques, *Journal of the Institution of public Health engineers India, special Issue on mine Environment, March- 2004, page- 236- 240.*
- [2] Singh K.K., Singh A.K. and Hasan S.H., 'Removal of lead from waste water using low cost Biosorbent wheat Bran', *Bio Resource Technology, 97, page 994 –1001, 2006, U.S.A.*
- [3] Qiming Y. U. and Pairat, K., 'Binary Adsorption of cu (II) and Cd (II) from aqueous solution by Biomass of Marine Alga *Durvillaea potatorum*, *J. of separation Science and Technology, 34 (8), pp – 1595- 1605, 1999*
- [4] Inow K., Chimire K.N., oshima. T and Hashimoto K. Removal of arsenic from mine water by effective use of Biomass, *I.M.M. Abstract, Vol. 54 (2), June 2004, page- 123, A 0401155.*
- [5] Adams D.I., Pennington. P. "Selenium and Arsenic removal from mining wastewaters", *I.M.M. Abstract, Vol 55 (3), sept. 2005, page 220, A0501937.*
- [6] Melegy A.A., Ishmael I.S. and Basti. Z, "A comparative Study of the adsorbed Pb (II), Cd (II) and Zn (II) on Smectite, Kaolinite and Illite using xps. *I.M.M. Abstract Vol. 55(4), December – 2005, page – 324 Ao5o2849.*
- [7] Yadav. K.P., Tyagi, B.S. and Singh, V.N. 'Effect of Temperature on the removal of lead (II) by adsorption on china clay and wollastonite, *J. chem. Tech and Biotechnology, Vol . 51, page 47- 60, 1991.*
- [8] Akar, T. and Junali, S., 'Biosorption performance of *Botrytis cinevea* fungal byproducts for removal of Cd(II) and Cu(II) ions from aqueous solutions, *I. M.M. Abstract, vol. 55 (4) December – 2005, page 324, No. Ao050 2843.*