



Batch-Wise Tungstate Removal From Water On A Surfactant-Modified Zeolite

Vandana Swarnkar^[1], Nishi Agrawal^[2], Priya pawaiya^[2a], Radha Tomar^[3]

School of Studies in Chemistry, Jiwaji University, Gwalior, M.P., India

ABSTARCT

Tungstate sorption kinetics were determined in batch-wise experiments on a surfactant-modified zeolite (SMZ), prepared by treatment of a clinoptilolite sample by HDTMA-Br (HDTMA being the hexadecyltrimethylammonium cation). The influence of various parameters was studied, namely pH, effect of temperature and initial Tungstate concentration with a maximal removal value at equilibrium of about 80%.

Key words: Surfactant modified Clinoptilolite, Batch, Water, HDTMA.

INTRODUCTION

To accurately characterize the ecotoxicity of sodium Tungstate for Registration, Evaluation and Authorization of Chemicals (REACH) [1] and classification, labeling, and packaging (CLP) [2], the Tungsten Consortium sponsored a coordinated series of terrestrial and aquatic toxicity tests. Results of the terrestrial tests with earthworms (*Eisenia fetida*) and three plant species (oat, *Avena sativa*; radish, *Raphanus sativus*; and lettuce, *Lactuca sativa*) are reported here. Tungsten speciation and behavior in the environment is fairly complex and is dependent on the characteristics of the environmental compartment in question. For example, soil sorption coefficients are found to increase with decreasing pH [3]. Additionally, soil-tungsten systems may take up to approximately three to four months to reach equilibrium [3,4]. Therefore, it is important to note that the mobility and, therefore, the bioavailability of tungsten can vary depending on environmental conditions, and it is necessary to define adequately the parameters used for ecotoxicity testing. Sodium Tungstate is known to be very soluble (73.2 g/cc [73.2g/ml] at 218C) [5] and is expected to represent adequately the worst-case toxicity for most tungsten compounds. Other studies examining toxicity of sodium Tungstate to terrestrial organisms [6,7] have found that tungsten compounds are only toxic to earthworms at relatively high concentrations. Toxicity was reported at slightly lower soil concentrations in sunflowers [8], which may indicate higher sensitivity in plants than terrestrial invertebrates. The present study thus aims to investigate the Tungstate ions sorption on clinoptilolite-based SMZ at room temperature through batch experiments.

MATERIALS AND METHODS

Sample preparation and Modification of Willhendersonite:

To synthesize analogues of Willhendersonite $\text{KCaAl}_3\text{Si}_{3.25}\text{H}_2\text{O}$, the metal ion potassium, calcium, aluminium and silicon were taken in the molar ratio 1: 1: 3: 3 respectively. They are used as their salt potassium nitrate, calcium nitrate, aluminium nitrate, tetra aminosilicate. The synthetic raw Willhendersonite were treated hexadecyltrimethylammonium bromide (HDTMA- Br) surfactant at a level 150 mmol/kg (42.6 HDTMA per kg of Willhendersonite) to synthesized the analogue of Willhendersonite. Each mixture was equilibrated on a water bath shaker at 150 rpm and 250°C for 8 hours. Then mixture was centrifuged and the supernatant solution analyzed. Zeolite was washed with to portions of type I distilled water and then air-dried.

Batch sorption tests:

Sorption isotherm was conducted by batch experiments at 20°C , pH 7.0. The experiments were carried out in 150ml stopper conical flasks containing 100ml of (Sodium Tungstate) solutions with concentration $1\text{--}35\text{ mg l}^{-1}$, with sorbent 0.1 g l^{-1} . To analyse the effects of pH, the equilibrium sorption of tungstate measured at different pH levels from 3 to 10 by setting the initial molybdenum concentration at 5 mg l^{-1} with sorbent 0.1 g l^{-1} . The initial pH of solution was adjust by 0.1 M HCL and NaOH solutes. The flasks were shaken at 180 rpm in a shaker for 24 hours and then the suspension was passed through a membrane filter ($0.45\mu\text{m}$) for analysis. Tungstate was analysed on an UV-Spectrophotometer. The initial Tungstate concentration was 10 mg l^{-1} , the sorbent was 1 g l^{-1} , and the initial pH was 7.0.

RESULTS AND DISCUSSIONS

Thermodynamic Studies

Thermodynamic parameters i.e. free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS), they all vary with the thermodynamic equilibrium constant (K) and were calculated using equation 1, 2 & 3. The negative value of ΔG indicates that the sorption of metal oxoanions on modified zeolite minerals is a spontaneous process. The positive value of enthalpy change (ΔH) confirms the endothermic sorption process. The positive value of ΔS suggests the increase in randomness at the solid solution interphase during sorption. The amount of metal oxoanion sorbed at equilibrium at different temperature has been utilized to evaluate the thermodynamic parameters for the sorption. The Van't Hoff plot of $\ln K$ V/s $1/T$ comes out to be straight line figure 6 for surfactant modified Willhendersonite respectively.

$$\Delta G^0 = -RT \ln K \text{ or } -2.303RT \log K \quad (1)$$

$$\log K_2/K_1 = \Delta H^0 / 2.303R [1/T_1 - 1/T_2] \quad (2)$$

$$\Delta S^0 = \Delta H^0 - \Delta G^0 / T \quad (3)$$

Effect of pH

Table 2: Effect of pH of the solution on sorption of metal oxoanions by surfactant modified Willhendersonite

Metal oxo anion	pH of the solution	Initial concn of metal oxoanion meq	Metal concn in solid phase meq	Metal oxoanion concn at equilibrium meq	Kd ml/gm	Sorption %
WO_4^{2-}	1	0.5005	0.0775	0.4225	91.71	15.5
	3	0.5005	0.1340	0.3660	183.06	26.8
	5	0.5005	0.2170	0.2830	383.39	43.4
	7	0.5005	0.3475	0.1525	1139.3	69.8

9	0.5005	0.2880	0.2120	679.24	57.6
---	--------	--------	--------	--------	------

Weight of ion exchanger: 100mg, Temperature : 250C, Equilibrium time: 7

CONCLUSION

The present study focuses on sorption of W(VI) from aqueous solutions using the Willhendersonite-surfactant modified zeolite composite as a low cost sorbent. The sorption characteristic has been examined with the variations in the parameters of concentration of W(VI), pH, temperature. The pH experiments showed that the governing factors affecting the sorption characteristics of sorbent. Sorption is relatively high at pH 7. This phenomenon can be explain by competition of the H⁺ ions with Tungstate ions at low pH values and precipitation of hydroxyl species onto the sorbents (pH 7- 9) at higher pH. Thermodynamic parameters revealed that the sorption process is exothermic and spontaneous with a increased randomness in nature.

REFERENCE

- [1]. Official Journal of the European Union. **2007**. Regulation (EC) No. 1907/2006 of the European Parliament and of the Council of 18 December **2006** concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC. Brussels, Belgium.
- [2]. Official Journal of the European Union. **2008**. Regulation (EC) No. 1272/ 2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/ EC, and amending Regulation (EC) 1907/2006. Brussels, Belgium.
- [3]. Bednar A.J., Jones W.T., Boyd R.E., Ringelberg D.B., Larson S.L.B., Geochemical parameters influencing tungsten mobility in soils. *J. Environ. Qual.*, **37**, 229–233, **(2008)**.
- [4]. Griggs C., Larson S., Johnson J., Felt D., Nestler C., Partitioning between aqueous and soil system components for soluble tungsten and lead species, *Land Contam Reclam*, **17**, 83–91, **(2009)**.
- [5]. Weast R.C., *Handbook of Chemistry and Physics* 56th ed. CRC, Cleveland, OH, USA, p B–145, **(1975)**.
- [6]. Strigul N., Galdun C., Vaccari L., Ryan T., Braidia W., Christodoulatos C., Influence of speciation on tungsten toxicity, *Desalination* **248**, 869–879, **(2009)**.
- [7]. Inouye L.S., Jones R.P., Bednar A.J., Tungsten effects on survival, growth, and reproduction in the earthworm, *Eisenia fetida*. *Environ. Toxicol. Chem.*, **25**, 763–768, **(2006)**.