

# USE OF WOLLASTONITE IN THE REMOVAL OF NI(II) FROM AQUEOUS SOLUTIONS

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**Abstract.** The ability of wollastonite to adsorb Ni (II) from water has been carried out. A removal of 92% of Ni (II) with 20 g L<sup>-1</sup> of adsorbent was observed at 50 mg L<sup>-1</sup> adsorbate concentration, 6.5 pH and 30 °C. The process follows a first order rate kinetics with diffusion controlled nature and the data fits the Langmuir adsorption isotherm. Removal of Ni increases from 10 to 92% with the rise of pH from 3.0 to 8.0 and thereafter it remains almost unchanged. This change has been explained on the basis of aqueous-complex formation and the subsequent acid base dissociation at the solid-solution interface.

## 1. Introduction

Nickel is widely distributed throughout the earth's crust and its principal ores are pentlandite, garnierite and the arsenicals NiAs and NiAs<sub>2</sub>. The discharges from electroplating, utensil manufacturing, metallurgical and catalytic processes increase the Ni (II) burden on the ecosystem and deteriorate water quality. European Economic Community (Sayre, 1988) has fixed the MCL (Maximum Contaminant Limit) for Ni in potable water as 50 µg L<sup>-1</sup>. Watras *et al.* (1985) found Ni to be acutely and chronically toxic for *Scenedesmus* and *Daphnia*. It is also harmful for bean and maize (Purvas, 1977). The hazardous nature of Ni is well documented and it has been found to be a potent carcinogen (Mukherjee, 1986).

Chemical precipitation has been a popular method (Patterson and Minear, 1975) for the removal of Ni from aqueous system. However, it requires an appropriate dosing of the precipitant and regular monitoring. An additional financial burden is incurred for the sludge disposal. Wollastonite is a cheap clay mineral ( $\alpha$ -calcium metasilicate,  $\alpha$ -CaSiO<sub>3</sub>) and is quite abundant in different parts of the world. Its estimated reserves in India alone are approximately 25 × 10<sup>6</sup> t (Panday, 1984). It is commonly used in preparing ceramic bodies and other materials but during recent years Jain *et al.* (1984) and Panday *et al.* (1986) have used this clay mineral as an adsorbent in water pollution control. Moreover, the adsorption technique is becoming a popular choice in water and wastewater treatment because of its low maintenance cost, simple design and easy operation. This paper deals with an attempt to utilize wollastonite as an adsorbent for the removal of Ni(II) and to replace the otherwise costly adsorbents like activated C etc.

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## 2. Experimental

All the chemicals used were of analytical reagent grade and were obtained from BDH. Wollastonite was supplied by M/s Wolkem Pvt. Ltd., Udaipur, India. In order to avoid extra expenditure it was used as received after being passed through 100  $\mu\text{m}$  sieve and analyzed chemically (Indian Standard Methods, 1960). The mineralogical analysis was carried out with the help of XRD method (Philips Diffraction Unit, Model PW 1710) using  $\text{Cu}\alpha$  radiations and IR Spectroscopy (Perkin Elmer, Spectrophotometer Model 621). The scanning speed was  $1^\circ \text{min}^{-1}$  during XRD analysis. The BET method (Powers, 1947) using a Quantasorb Surface Area Analyzer, Model QS-7 (Quanta-Chrome Corp. U.S.A.) was used to measure the surface area.  $\text{pH}_{\text{ZPC}}$  was determined by electrophoretic method using a Lazer zee Meter, Model 500 (Penkem, Inc., New York, USA) (Panday *et al.*, 1985). Porosity was measured by the mercury intrusion method employing a Carlo Erba series 200 Porosimeter (Raman and Venkatnarayan, 1971) and the Rees-Hugill Flask Method (Chesters, 1983) was used for the determination of the density of the sample. Batch adsorption experiments were conducted at 30  $^\circ\text{C}$  by agitating 1.0 g of wollastonite with 50 mL aqueous solution of Ni (II) of desired concentrations and pH in different polythene bottles in a shaking thermostat machine. The shaking speed was 125 rpm throughout the study. After a fixed period of agitation, the solutions were centrifuged at 5000 r.p.m. The concentration of Ni ions in the supernatant was determined using Atomic Absorption Spectrophotometer (Perkin Elmer Model 312). Data for the isotherm were obtained by allowing the adsorbent to remain in contact with solution for the time, necessary to attain equilibrium. Ionic strength was maintained at 0.01 M  $\text{NaClO}_4$ .

## 3. Results and Discussion

### 3.1. CHARACTERIZATION OF WOLLASTONITE

The chemical characterization of wollastonite shows the presence of mainly  $\text{SiO}_2$ ,  $\text{CaO}$  and other oxides in traces (Table I). It may be expected that Ni (II) species will be removed mainly by  $\text{SiO}_2$  and/or  $\text{CaO}$ . The mineralogical analysis (Tables II and III) indicates the dominance of wollastonite with traces of mullite, hematite and quartz. The appearance of the band at  $1160 \text{ cm}^{-1}$  indicates the presence of bentonite in wollastonite and the absorption bands at 1105, 1075, 1050, 660 and  $635 \text{ cm}^{-1}$  are indicative of wollastonite mineral (Hunt *et al.*, 1950). Emissions appearing at 890, 335, and  $310 \text{ cm}^{-1}$  show the presence of  $\text{CaO}$  (Tuddenham and Lyon, 1960). Some weak to medium emissions were also observed in the spectrum of wollastonite which do not provide any information about the occurrence of other minerals. However, the specific absorption bands at 1010, 715, and  $625 \text{ cm}^{-1}$  show the presence of traces of mullite (Marel and Bentelspacher, 1976) and hematite (Gadsen, 1975). The strong bands at 470 and  $440 \text{ cm}^{-1}$  illustrate the presence of

TABLE I  
Chemical characterization of wollastonite

Constituents	% by weight
SiO <sub>2</sub>	48.52
CaO	48.48
Fe <sub>2</sub> O <sub>3</sub>	0.26
Al <sub>2</sub> O <sub>3</sub>	0.24
Loss on Ignition	2.50
Mean particle diameter	48 × 10 <sup>-4</sup> cm
Surface area	1.18 m <sup>2</sup> g <sup>-1</sup>
Porosity	0.23
Density	2.21 g cm <sup>-3</sup>
pH <sub>ZPC</sub>	2.60

TABLE II  
Important I.R. bands of wollastonite along with their possible assignments

Band	position	Assignment
1160	m	Si - O stretch
1105	Sh	Si - O stretch
1075	s	Si - O - Si stretch
1050	s	Si - O - Si stretch
1010	w	Si - O - Al stretch
890	s	Ca - O - stretch
715	m	Si - O - Fe(Al)
660	s	Si - O - Ca stretch
615	s	Si - O - Al stretch
565	s	Si - O bend
505	sh	Si - O bend
470	s	Si - O - Ca bend
440	s	Si - O bend
385	m	Si - O bend
335	w	Ca - O bend
310	w	Ca - O bend

s = strong, m = medium, Sh = shoulder, w = weak.

kaolinite and the bands at 505 and 385 cm<sup>-1</sup> characterize quartz (Marel and Bentelspacher, 1976). Gibbsite (Marel and Bentelspacher, 1976) in small quantities in wollastonite is indicated by the absorption band at 505 cm<sup>-1</sup>. These results are supported by the findings of some earlier workers (Saksena *et al.*, 1963; Lazarer, 1972). It is clear from the XRD analysis results (Table III) that mineral wollastonite was the major phase (ASTM Card No. 2-0689, ASTM Card No. 3-0626). In addition, occurrence of some other minerals like kaolinite (Brindley and Robinson, 1948), gibbsite (ASTM Card No. 1-0263), calcite (Donnay and Ondik, 1973),  $\alpha$ -quartz

TABLE III  
X-ray diffraction, 'd' values of wollastonite

d (Å)	Possible mineral
3.8271	$\beta$ - Wollastonite
3.0150	$\beta$ - Wollastonite
2.8259	Wollastonite
1.9042	Wollastonite
1.2933	Wollastonite
2.4821	Kaolinite
2.2733	Kaolinite
2.0856	Gibbsite
1.8677	Calcite
1.6198	$\alpha$ - Quartz
1.4165	$\alpha$ - Quartz
1.5984	Hematite
1.3345	Hematite
1.5191	Mullite
1.4360	Bohemite

and hematite (Berry and Thomson, 1962), mullite (ASTM Card No. 2-0430) and bohemite (ASTM Card No. 5-0190) was also recognized.

### 3.2. EFFECT OF CONCENTRATION

Figure 1 shows the effect of concentration on the removal of Ni (II) by adsorption

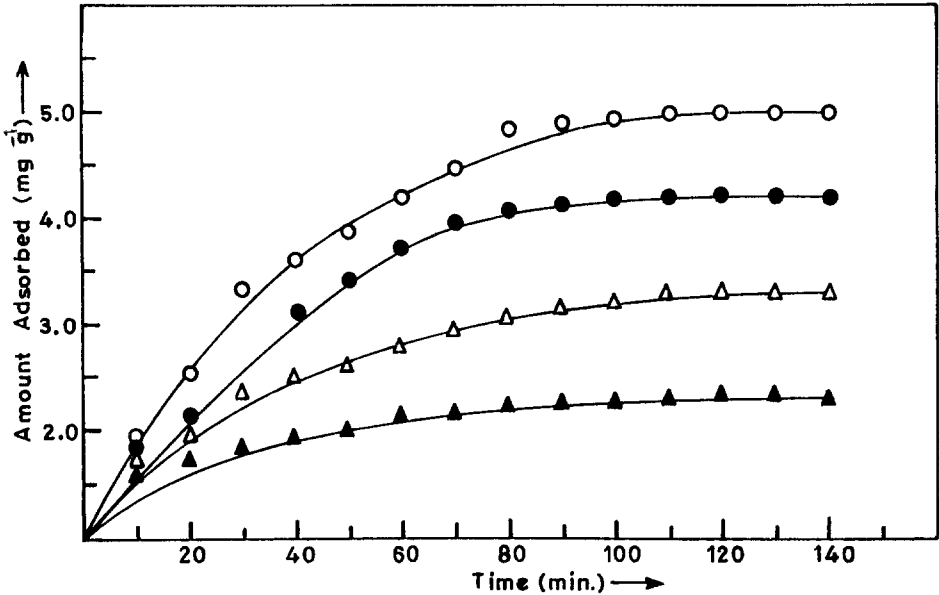


Fig. 1. Effect of time and concentration on Ni (II) removal by adsorption on wollastonite. Temperature = 30 °C, pH = 6.5, Concentrations: (▲) 50 mg L<sup>-1</sup>, (△) 75 mg L<sup>-1</sup>, (●) 100 mg L<sup>-1</sup> and (○) 125 mg L<sup>-1</sup>, Ionic strength = 0.01 M NaClO<sub>4</sub>.

on wollastonite. It is clear from Figure 1 that the uptake of Ni (II) increases slowly with the lapse of time and reaches to saturation in 110 min. With the change in concentration of the solution from 50 to 125 mg L<sup>-1</sup>, the percentage removal of Ni (II) decreased from 92 to 79%. The percentage uptake is highly dependent on initial concentration ( $C_i$ ) of the Ni (II) ions in the solution (Figure 2). It can be concluded that high removal at low concentration is important in terms of industrial application.

### 3.3. ADSORPTION KINETICS

The adsorption of Ni (II) on wollastonite follows the first order adsorption rate expression of Lagergren (1898):

$$\log(q_e - q) = \log q_e - (k/2.3) \cdot t \quad (1)$$

where  $q_e$  and  $q$  (both in mg g<sup>-1</sup>) are the amounts of Ni (II) ions adsorbed at equilibrium

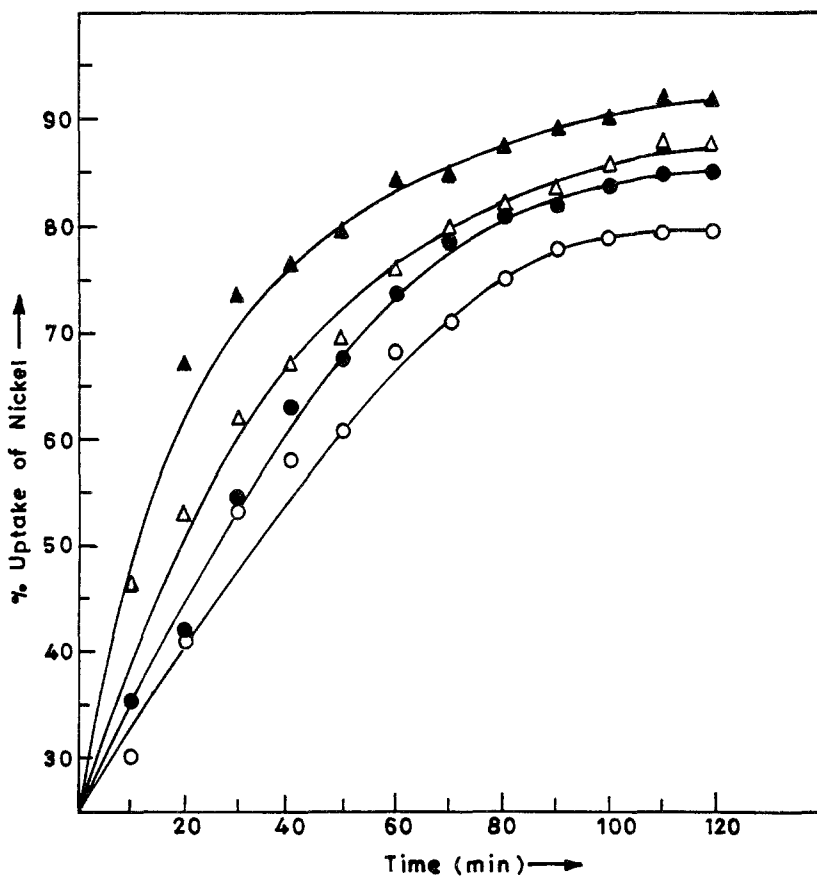


Fig. 2. Percentage uptake of Ni (II) by adsorption on wollastonite, Temperature = 30 °C, pH = 6.5, Concentrations: (▲) 50 mg L<sup>-1</sup> (Δ) 75 mg L<sup>-1</sup>, (●) 100 mg L<sup>-1</sup> and (○) 125 mg L<sup>-1</sup>, Ionic strength = 0.01 M NaClO<sub>4</sub>.

and at any time,  $t$ , respectively. The linear plot of  $\log (q_e - q)$  vs  $t$  at 30 °C (Figure 3) indicates the validity of the above equation for the present system. The adsorption rate constant,  $k$ , has been determined graphically and found to be  $1.02 \times 10^{-2} \text{ min}^{-1/2}$  at 30 °C. Similar studies regarding kinetics and equilibrium for metal adsorption have also been performed by Dzombak and Morel (1986) and Schindter and Stumm (1988).

### 3.4. ADSORPTION ISOTHERM

The adsorption data for the studied range (i.e., 50 to 125 mg L<sup>-1</sup>) fits rearranged Langmuir Isotherm:

$$\frac{C}{q} = \frac{1}{q_{\max} b} + \frac{C}{q_{\max}}, \quad (2)$$

where,  $q_{\max}$  (mg g<sup>-1</sup>) and  $b$  (L mg<sup>-1</sup>) are the Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The plot of  $C/q$  Vs  $c$  at 30 °C (Figure 4) is linear indicating the formation of monolayer coverage for the present study. The values of  $q_{\max}$  and  $b$  were determined graphically and confirmed by regression analysis and found to be 6.52 mg g<sup>-1</sup> and 0.128 L mg<sup>-1</sup>, respectively.

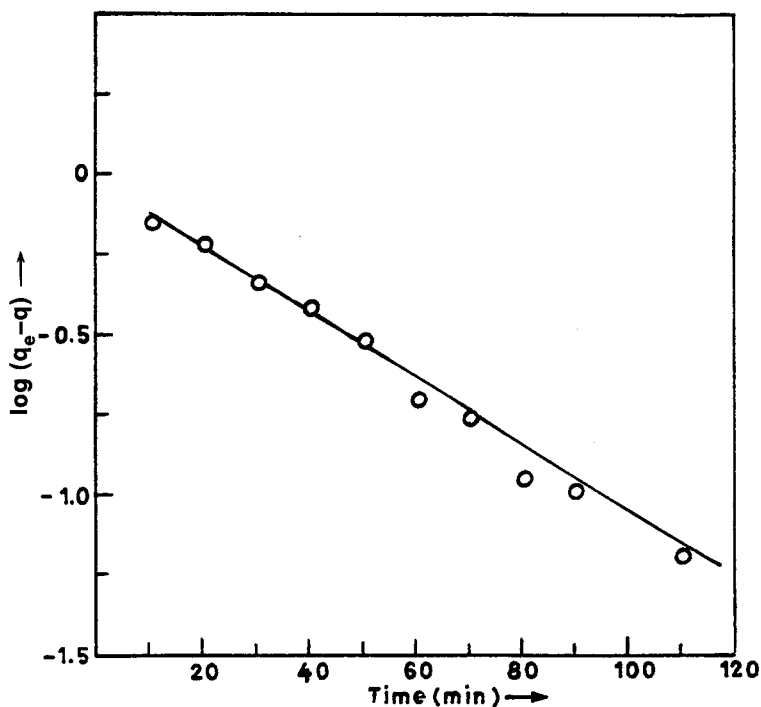


Fig. 3. Kinetics of Ni (II) removal by adsorption on wolastonite: Lagergren plot. Temperature = 30 °C, pH = 6.5, Concentration = 50 mg L<sup>-1</sup>, Ionic strength = 0.01 M NaClO<sub>4</sub>.

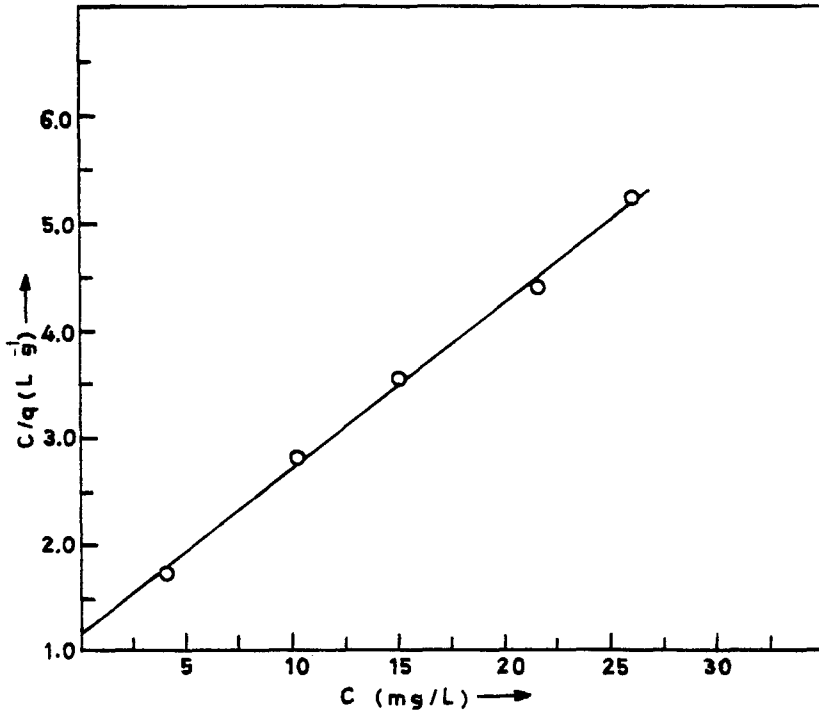
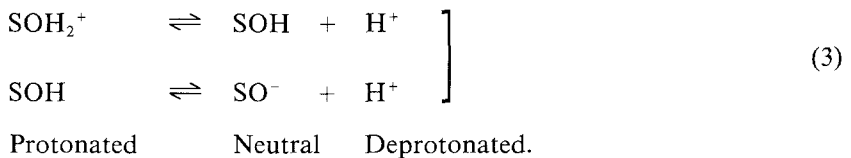


Fig. 4. Langmuir plot for removal of Ni (II) by adsorption on wollastonite, Temperature = 30 °C, pH = 6.5, Ionic strength = 0.01 M NaClO<sub>4</sub>.

### 3.5. EFFECT OF pH

The uptake of Ni (II) was accompanied by the decrease of pH. The removal was small in the acidic range, rises sharply between pH 6 to 8 which may be referred to the 'pH adsorption edge' and attains a maximum value around pH 8 (Figure 5). Similar results have also been reported by Schultz *et al.* (1987) for the adsorption of Ni (II) on ferrihydrite (Figure 6). This may be explained on the basis of physico-chemical properties at the solid-liquid interface.

According to Mouvet and Bourg (1981), Ni<sup>2+</sup> is the only important oxidation state in aqueous chemistry of Ni and is generally present as Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> (Cotton and Wilkinson, 1962). The oxide water interface may be schematically shown as under



It is expected that protonated surface would not favor Ni (II) adsorption and the uptake would be increased in the alkaline range. This is born out in our investigations.

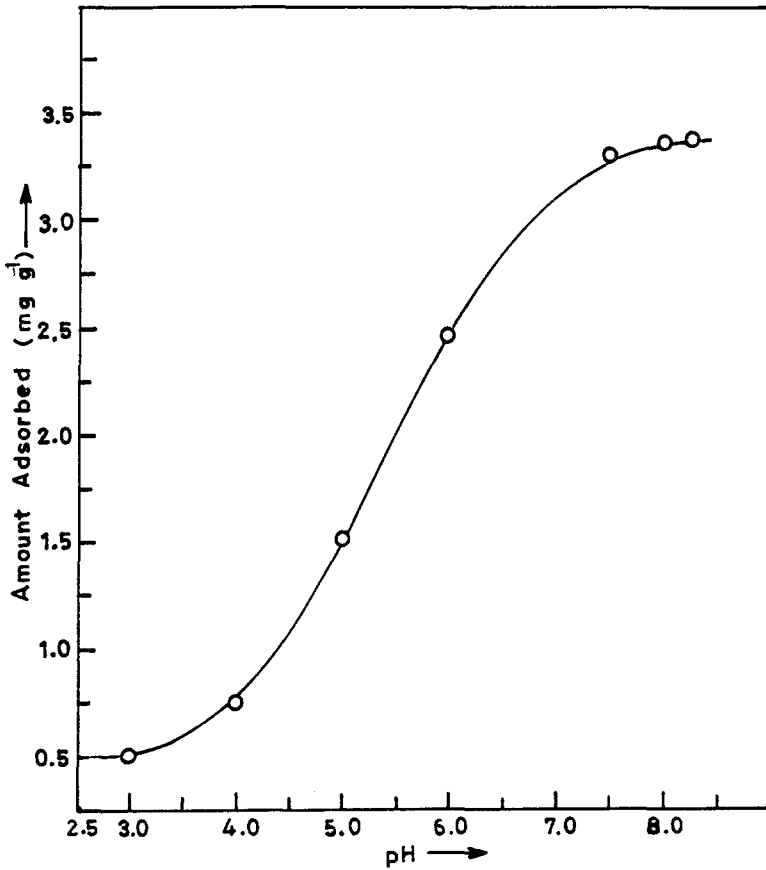
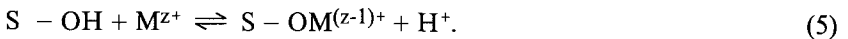
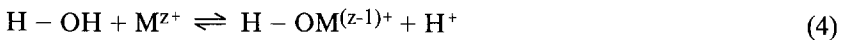


Fig. 5. Effect of pH on the removal of Ni (II) by adsorption on wollastonite. Temperature = 30 °C, Concentration = 50 mg L<sup>-1</sup>, Ionic strength = 0.01 M NaClO<sub>4</sub>.

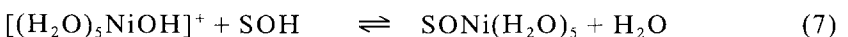
The following hydrolysis (4) and complexation (5) reactions are expected at the surface of the adsorbent.



pH value is a master variable that governs the extent of adsorption for the given system consisting of metal ions Ni (II) and on adsorbing (hydr) oxide. The extent of adsorption rises considerably between the pH range 5.0 to 7.0. The metal competes with H<sup>+</sup> for surface sites.



These equations form the basis of the surface complexation model (Stumm, 1987)





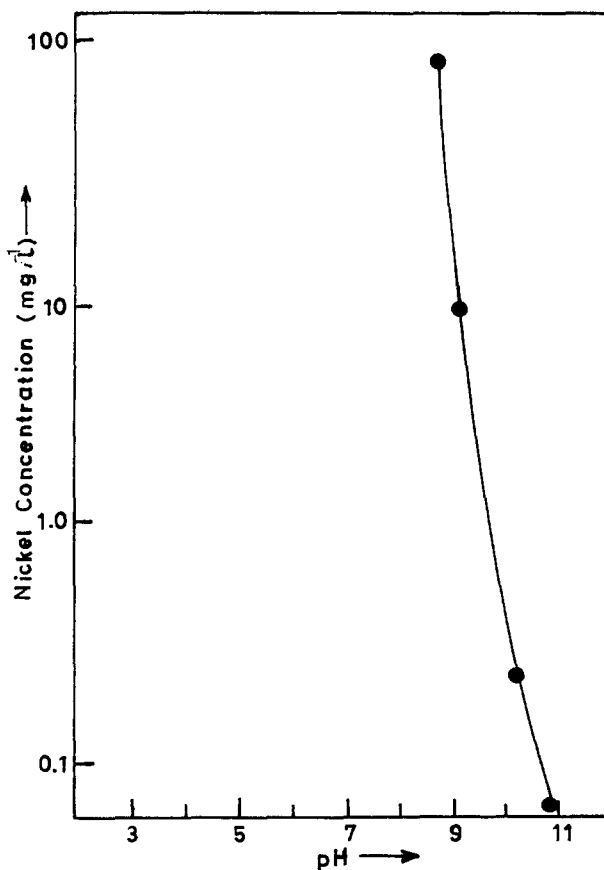
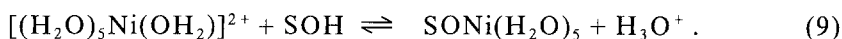
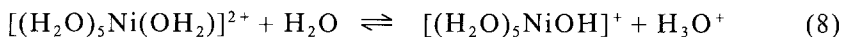


Fig. 6. Plot showing pH dependence of removal of Ni (II) by adsorption on wollastonite, Temperature = 30 °C, pH = 6.5, Concentration = 50 mg L<sup>-1</sup>,  $n = 2.2$ .



However, a competition between metal ions and  $\text{H}^+$  ( $\text{M}^{++} - \text{H}^+$ ) for surface sites cannot be ruled out. Simple analysis of pH dependence of Ni (II) adsorption under the present experimental conditions has been carried out. A linear plot of  $\log q_e$  vs  $(\log C + n' \text{pH})$  or  $C_{\text{Ni}}/C_{\text{H}}^n$  was obtained (Figure 7).

The following empirical relationship for pH dependence of Ni (II) adsorption has been developed.

$$\log q_e = A + (\log C + n \text{pH}) . \quad (10)$$

$A$  and  $n$  are constants and their values were calculated from the linear plot (Figure 7) and we got  $A = 0.06$  and  $n = 2.2$  for the present system. Substituting numerical value Equation (10) reduces to

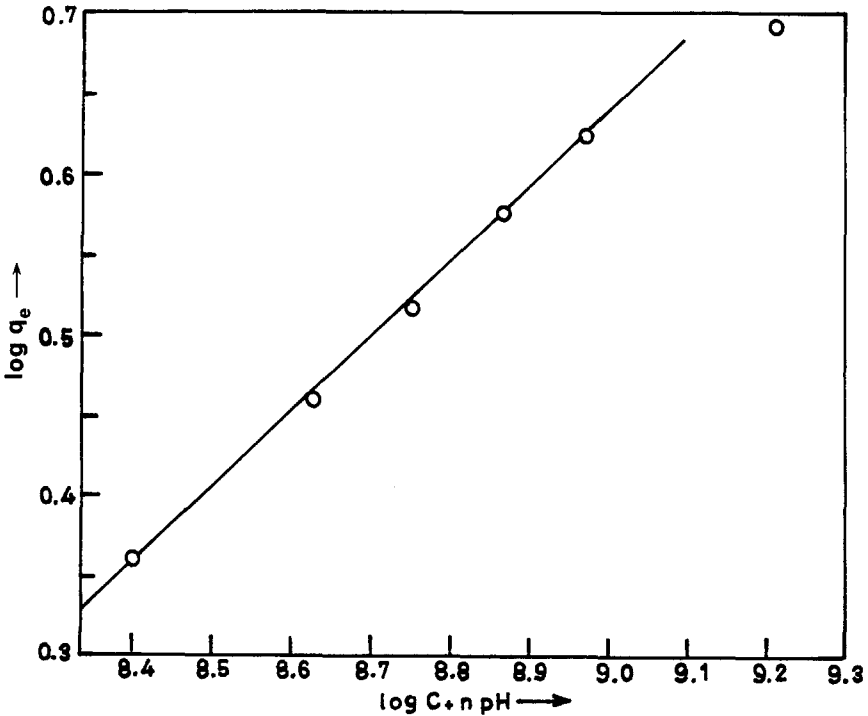


Fig. 7. Plot showing precipitation of nickel hydroxide as a function of pH. Temperature = 30 °C. Concentration = 50 mg L<sup>-1</sup>, Ionic strength = 0.01 M NaClO<sub>4</sub>.

$$\log q_e = 0.06 + (\log C + 2.2 \text{ pH}) . \quad (11)$$

#### 4. Conclusion

- (1) Higher uptakes (92% of Ni (II)) from aqueous solution is possible using wollastonite as an adsorbent provided the initial concentration of the Ni (II) in the effluent is low. This is our important finding in the light of industrial applications.
- (2) The adsorption follows the first order kinetics.
- (3) The adsorption data fits the rearranged Langmuir isotherm under the present experimental conditions.
- (4) pH has been found to be a master variable controlling the adsorption of Ni (II) by the oxides present in wollastonite. The adsorption behavior can be predicted ( $q_{\max}$ ) from a knowledge of  $C_{\text{Ni}}/C_{\text{H}}^n$  ratio, where 'n' is equal to 2.2 under the present conditions. The adsorption is maximum around pH 8.0 onwards and it has been concluded that surface complexation involving H<sup>+</sup> exchange and chemical precipitation contribute towards maximum uptake.
- (5) The data, thus obtained, may prove to be a blue chip for Ni (II) removal from wastewater using batch or stirred-tank flow reactors.

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