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Adsorption of Hexavalent Chromium onto Raw Vermiculite Grades as a Function of Solution Concentration

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Abstract: The work was aimed to evaluate the adsorption of Cr on raw vermiculite grades 1 to 5 as a function of solution concentration onto raw vermiculites from Tamil Nadu Minerals Limited (TAMIN),Chennai, India. The various raw vermiculite grades from 1 to 5 exhibited a rapid instantaneous adsorption of Cr among which raw vermiculites grade 2 tops the list with 97.4 per cent removal of Cr from 250 mg L^{-1} of the equilibrium solution. In all the grades of raw vermiculites, the pH of the equilibrium solution decreased as a result of removal of Cr from solution.

Keywords: Raw vermiculite grades, Hexavalent chromium, Adsorption, Batch experiments

INTRODUCTION

Vermiculite is the geological name given to a group of hydrated laminar minerals that are magnesium – aluminum – iron silicates with a suggested formula of (Mg, Fe^{+2}, Al)$_3$ (Al, Si)$_4$ O_{10} $(OH)_2$. $4H_2O$[1]. Vermiculite is the member of the phyllosilicate mineral group and is micaceous in nature. Flakes of raw vermiculite concentrate are mica-like in appearance and contain water molecules within their internal surface. When the flakes are heated rapidly at a temperature of 1000°C or higher, the water flakes into steam, and the flakes expand into accordion like particles. The word "vermiculite" is derived from the Latin word meaning "to breed worms", alluding to the worm-like shape resulting from its expansion on heating. This expansion process is called exfoliation, and the resulting light weight material is chemically inert, fire resistant and odourless. Vermiculite can absorb such liquids as fertilizers, herbicides and insecticides which can then be transported as free-flowing solids[2].

Tanning industry is one of the important industries in India, which earns considerable foreign exchange through the leather export. There are about 5000 tanneries in India. The quantity of effluent released from the tanneries is about 50 to 60 litres per kilogram of leather tanned. The tannery wastes are ranked as high pollutants among the industrial wastes .Tannery effluent is rich in salt content especially the chromium. Chromium in its hexavalent form is one of the undesirable heavy metals because it affects human physiology, accumulates in the food chain and causes several ailments[3].

The trivalent form is relatively innocuous, but hexavalent chromium is toxic, carcinogenic and mutagenic in nature, highly mobile in soil and aquatic system and also is a strong oxidant capable of being adsorbed by the skin[4]. So the removal of Cr (VI) besides colour, sodium, calcium, magnesium salts from tannery effluents is important before discharging them into aquatic environments or on to land.

A wide range of physical and chemical processes are available for the removal of Cr (VI) and salts from tannery effluents include chemical precipitation, reverse osmosis, evaporation, ion exchange and adsorption. Adsorption on activated carbon (ARC) has been adopted as tertiary treatment in various types of industries because of its excellent adsorption capability[5]. However, it's use is limited by its high cost[6]. In this context, vermiculite mineral with its high cation exchange capacity and reactive surface area was scientifically evaluated for its potential to substitute the activated carbon which could be cost effective and economically feasible treatment method. Hence, a detailed investigation was undertaken to evaluate the adsorption of Cr on raw vermiculite grades 1 to 5 as a function of solution concentration.

MATERIALS AND METHODS

Ten categories of vermiculites, the 2:1 type of alumino-silicate clay mineral, obtained from Tamil Nadu Minerals Ltd., Chennai, India was used in this

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study. Vermiculite is a hydrated silicate, which are graded accordingly to specific sizes. The specific sizes for the five raw vermiculite grades are detailed below.

Vermiculite types	Grade	Size
Raw	I	More than 12mm (½" and above)
Raw	II	6mm –12mm (¼" to ½")
Raw	III	3mm – 6mm (1/8" to ¼")
Raw	IV	1mm – 3mm (1/20" to 1/8")
Raw	V	Fines (below 1mm) < 1/20"

Adsorption as a Function of Solution Concentration: The adsorption of Cr as a function of solution concentration was evaluated by taking 30 ml of Cr (VI) solutions at varying concentrations *viz.,* 250, 500, 750 and 1000 mg Cr L^{-1} in 100ml screw top polypropylene shaking bottles containing two gram of different grades of vermiculite. After the pH measurement, the mixtures were shaken thoroughly for a predetermined period of 12 hours, centrifuged (8000 rpm; 10 min) and filtered (Whatman No.1). The extracts were then analysed for pH and Cr concentration.

RESULTS AND DISCUSSIONS

Adsorption of Cr on Raw Vermiculites Grades 1 to 5 as a Function of Solution Concentration (table 1; Fig.1): Under various solution (Cr VI) concentrations, among the grades 1 to 5, the amount of Cr adsorbed

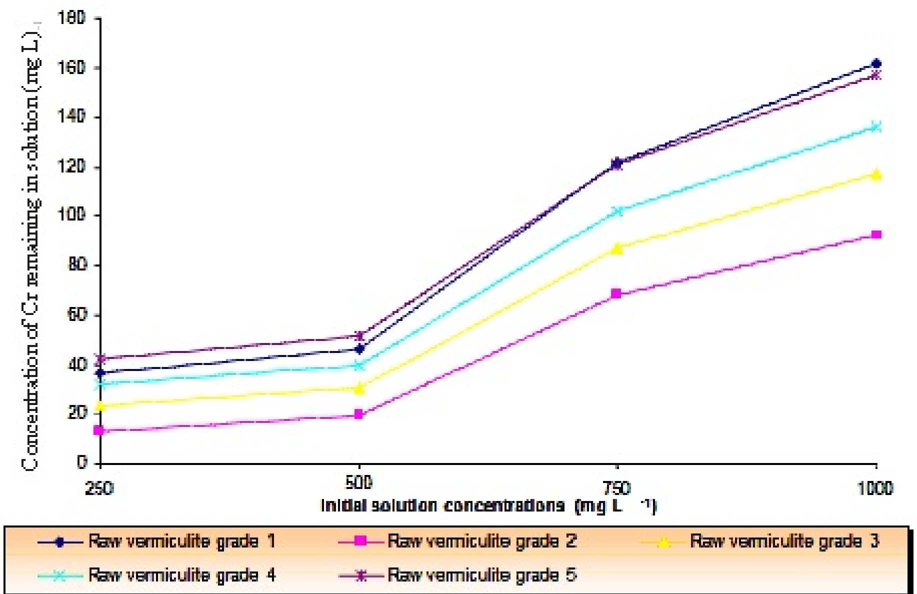

Fig. 1: Adsorption of Cr as a function of initial solution concentration for raw vermiculates grade (1 to 5).

ranged from 5145 mg kg^{-1} from 1000 mg L^{-1} solution concentration by grade 5 to 7305 mg kg^{-1} from 250 mg L^{-1} solution concentration by grade 2. The pH of the solution was found increased in all the solution concentrations after adsorption from its original value except grade 5 where it showed decreasing trend. The lowest percentage of Cr adsorbed was in grade 1 at 1000 mg L^{-1} solution concentration 67.6 per cent and the highest percentage was registered in grade 2 at 250 mg L^{-1} solution concentration 97.4 per cent.

Adsorption of Chromium as a Function of Solution of Cr (Vi) Concentration: The percentage removal of Cr as a function of initial Cr solution concentration (Fig. 2) increased with decrease in Cr concentration in equilibrium solution. The maximum adsorption among raw vermiculite grades occurred at 250 mg L^{-1}. Raw vermiculites, grade 2 tops the list with 97.4 per cent removal of Cr from 250 mg L^{-1} of the equilibrium solution. The higher adsorption capacity of RVG_2 may be attributed to its higher CEC (112c mol ($^{+}$) kg^{-1}) and its total surface area (42.0 gm^{-2}) than the other grades. The adsorption of clay mineral was confirmed by the findings of Atanassova[7]. The vermiculites grade is seen to be fairly active adsorbent even at higher initial concentration. The chromium removal of over 70 to 98% is obtained within the wide concentration range investigated. This obviously proved that the percentage adsorbed is dependent on initial concentration because the adsorption sites adsorbed the available chromium

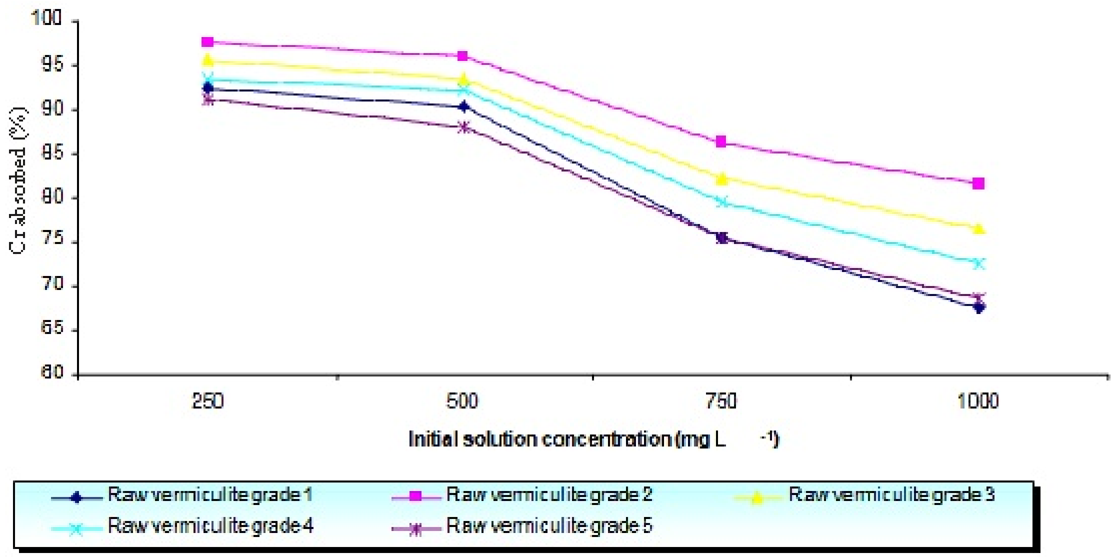

Fig. 2: Absorption of Cr on raw vermiculite grades (1 to 5) as a function of initial solution concentration.

more quickly at low solute concentration. However, for higher concentration, intra particle diffusion could be the predominant adsorption mechanism. Results indicated that all the grades of vermiculites performed consistently better in Cr removal at all levels. This is primarily due to the particle size and larger surface area of vermiculites grades.

In general, the amount of chromium adsorbed (and hence the percentage removal of chromium) increased with increase in the solute concentration the being 97.4 per cent for 250 mg L^{-1}, 96.1 per cent for 500 mg L^{-1}, 86.4 per cent for 750 mg $L^{-1}$and 81.6 per cent for 1000 mg L^{-1} (RVG_2). This might be due to the increase in number of sites. This is in line with the findings of Admson[8]. The results of the present study in these aspects corroborate with the findings of Paul *et al.,*[9] who inferred that at lower doses, the significant variations of percentage removal of chromium was possibly due to the saturation of surface active sizes with adsorbents molecules. Ainsworth *et al.*,[10] reported that the rate of Cr adsorption for the ten different soil types decreased with increasing levels of added Cr. Such behaviour might be due to decrease in fractions adsorption with increasing chromate concentration.

Summary and Conclusion: Adsorption is one of the efficient processes for treatment and an important phenomenon for removing Cr from different industrial wastewaters. Using laboratory batch experiment, adsorption maxima potential of different raw vermiculite grades were evaluated. All the grades of vermiculites performed consistently better in Cr removal at all levels. Raw vermiculite grade 2 removed 97.4 per cent of Cr from 250 mg L^{-1} of the equilibrium solution proved to be an efficient candidate for the removal of chromium.

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Table 1: Adsorption of Cr on raw vermiculite grades (1 to 5) at different initial chromium solution concentrations.

Concen-tration of Cr added (mgL-1)	Raw vermiculite's Grade 1 pH Before adsorption	After adsorption	Residual concentra -tion (mgL-1)	Concent-tration Cr adsorbed (mg kg-1)	Grade 2 pH Before adsorption	After adsorption	Residual concentra-tion (mgL-1)	Concent-tration Cr adsorbed (mg kg-1)	Grade 3 pH Before adsorption	After adsorption	Residual concentra-tion (mgL-1)	Concent-tration Cr adsorbed (mg kg-1)	Grade 4 pH Before adsorption	After adsorption	Residual concentra-tion (mgL-1)	Concent-tration Cr adsorbed (mg kg-1)	Grade 5 pH Before adsorption	After adsorption	Residual concentra-tion (mgL-1)	Concent-tration Cr adsorbed (mg kg-1)
250	5.01	5.18	36.9	6947 (92.6)	5.18	5.32	13	7305 (97.4)	4.98	5.06	23.6	7146 (95.3)	5.32	6.12	32	7146 (93.6)	6.23	5.98	42.5	6863 (91.5)
500	5.23	5.56	46.6	6801 (90.7)	5.06	5.42	19.6	7206 (96.1)	5.12	5.23	30.8	7038 (93.8)	5.46	5.82	40	6900 (92)	6.48	5.71	51.4	6729 (89.7)
750	5.41	5.73	122	5670 (75.6)	5.01	5.39	67.8	6483 (86.4)	5.19	5.43	87.2	6192 (82.6)	5.76	5.92	102	5970 (79.6)	6.32	5.63	121	5685 (75.8)
1000	5.68	5.93	162	5070 (67.6)	5.26	5.96	92	6120 (81.6)	6.01	6.24	117	5745 (76.6)	6.32	6.49	136	5460 (72.8)	6.59	7.21	157	5145 (68.6)

Values in parenthesis are percentage of Cr adsorbed for which statistical analysis have been done

	SEd	CD (0.05)	SEd	CD (0.05)	SEd	CD (0.05)	SEd	CD (0.05) SEd	CD (0.05)		
C x A	0.29	0.66	0.24	0.55	0.29	0.69	0.34	0.78	0.63	1.46	