Fast Removal of Chromium from Industrial Effluents Using a Natural Mineral Mixture

S. Ahmad[a]; I. H. Qureshi[a]

[a] Nuclear Chemistry Division, Pakistan Institute of Nuclear Science and Technology, Islamabad, Pakistan

PLEASE SCROLL DOWN FOR ARTICLE

FAST REMOVAL OF CHROMIUM FROM INDUSTRIAL EFFLUENTS USING A NATURAL MINERAL MIXTURE

S. AHMAD and I. H. QURESHI

Nuclear Chemistry Division, Pakistan Institute of Nuclear Science and Technology, P.O. Nilore, Islamabad, Pakistan.

The use of a naturally available mineral mixture (MM) for the removal of chromium from industrial effluents has been investigated. Adsorption of chromium on MM from aqueous solutions is reported, and the effect of equilibration time, temperature, hydrogen ions, adsorbent and adsorbate concentration and foreign ions is discussed. The contact time required is less than 10 min and the adsorption capacity is 45 g/kg of sorbent.

KEY WORDS: Chromium, toxicity, adsorption, natural minerals, environmental pollution

INTRODUCTION

The pollution of the biosphere by different toxic elements with their influx or release from various activities of man is of global concern. The pollutants find their way into the human body through the food chain, water and the atmosphere and may accumulate in vital organs and, subsequently, interfere in the normal biochemical functions. It is known that chromium at higher concentration levels is injurious to health: it induces mucodermal ulceration, cancer of the respiratory tract and allergic dermatitis of the skin.[1] The main contributing industries are the mining, metal plating, chemical pigments, leather tanning and textile industries.

Many procedures for the decontamination of chromium have been reported, such as reduction with sodium bisulphite, ferrous sulphate and hydrazine and, then, precipitation with lime or caustic soda and, further, reduction through ion exchange or by other adsorbents. These methods are expensive and time-consuming. Electrochemical treatment, adsorption with a flyash and wallastonite mixture and activated carbon have also been reported.[2-5] In our earlier communication, the adsorption of ^{90}Sr, ^{134}Cs and ^{137}Cs radionuclides has been investigated.[6] The behaviour of Cr in soil and water systems has also been investigated.[7-9] The landfill disposal of Cr wastes represents a potential hazard due to mobility in the soil. High concentrations of Cr in the middle zone of lateritic profiles all over the world are evidence of its mobility.[10] In the present study, the adsorption of chromium on a locally available naturally occurring mineral mixture (MM) was investigated. In addition to its good sorption properties, MM has considerable economical importance because of its low cost and abundant availability. The results on sorption

257

Table 1 Minerals in mineral mixture (MM)

Geothite	FeOOH (HFeO$_2$)
Hematite	Fe$_2$O$_3$
Limonite	2Fe$_2$O$_3 \cdot$ 3H$_3$O FeO(OH)n H$_2$O
Magnetite	Fe$_3$O$_4$
Quartz	SiO$_2$
Diaspore	HAlO$_2$
Enstatite	Mg$_2$(Si_2O_6)
Saprolite	
Ilmenite	FeTiO$_3$
Olivine	MgFeSiO$_4$
Dolomite	Ca-MgCO$_3$
Bauxite	$Al_2O_3 \cdot 2H_2O$

behaviour of ^{51}Cr using MM were sufficient to define the optimum physicochemical conditions for the removal of Cr from industrial waste effluents and to demonstrate its usefulness in the economical designing of a decontaminating plant.

EXPERIMENTAL

Natural material used

The experiments were performed with a locally available natural mineral mixture containing the minerals given in Table 1. The mineral constituents were determined by optical microscopy and X-ray diffraction techniques.[11] The chemical composition was established using INAA and AES;[12-13] the element concentrations are given in Table 2. The mineral mixture (MM) was ground and sieved to achieve a particle size of 100–300 mesh (0.44–1.0 mm fraction) and was used without any pretreatment, so that natural conditions were simulated as far as possible.

Table 2 Chemical composition of mineral mixture (MM)

Element	Per cent
Fe	134–41
MgO	6.3–10.5
Al	4.8–9.3
SiO$_2$	18.5–29.1
Zn	0.14–0.080
Ca	4.23–16.4
Mn	0.51–0.83
Ni	0.31–0.55
Cu	0.07–0.09
Cr	0.35–0.52
Co	0.05–0.08
Ti	0.83–1.89

Reagents and radiotracer

All reagents used in this study were of laboratory-equivalent grade. The radiotracer ^{51}Cr was prepared locally by irradiating spec-pure chromium oxide with thermal neutrons in a PARR-I research reactor in our institute with a flux of 2×10^{13} n·cm^{-2}s^{-1} for an appropriate time. After a suitable cooling time, the target was dissolved in HNO_3 and 20% Cr_2O_3 stock solution was prepared.

Sorption measurement

Sorption was measured by equilibrating a known weight of the solid adsorbent (MM) with various aqueous solutions containing 10 μl(10^4 cpm) of stock radiotracer solution for a specific time. The solution was centrifuged at 5000 rpm for phase separation. The supernant solution was withdrawn and its activity was compared with the activity on the sorbent (solid) to calculate the adsorption percentage. The activities were measured with a well-type scintillation counter. The pH of all systems was measured using a glass electrode connected with a Pye model-97 pH meter.

RESULTS AND DISCUSSION

The physicochemical conditions and adsorption efficiency of chromium on MM were evaluated as a function of equilibration time (contact time), stirring time, temperature, grain size, pH, concentration of electrolytes, adsorbent concentration and amount of Cr. The influence of pH is important because it regulates the release of free metal ions from bound chemical forms in the natural water system, and the pH also controls the adsorption of the metal at the oxide-water interface.[14] Therefore, the adsorption of Cr was investigated from solutions of pH 1–14. The results shown in Figure 1 indicate that the per cent adsorption increases with an increase in pH of the aqueous solution and attains an almost 100% value from pH 7–10. A decrease of sorption at very high pH is probably due to the formation of colloidal species[15] which do not undergo sedimentation completely.

The electrolyte concentration has a strong effect on the compact layer and diffuse layer potential.[16] Chemical treatment of oxides tends to cause changes in surface properties. Therefore, adsorption of Cr was examined from solutions containing different electrolytes, namely HNO_3, $HClO_4$, H_2SO_4 and HCl, as a function of their concentration. The results shown in Figure 2 indicate that adsorption decreases with an increase in acid concentration. Chromium exhibits maximum adsorption at an acid concentration of 0.01 M. It has been reported that certain elements produce positively charged colloidal species upon hydrolysis in aqueous medium, while mineral iron(III) oxide and iron(III) hydroxides which are present as major components of MM possess a negative surface charge at low pH.[17] It is therefore possible to postulate that fixation may be mainly attributed to mutual attraction of positively charged ionic species and a negatively charged mineral surface. The adsorption at higher acidity is less. It may be due to competition between the excess H^+ in the
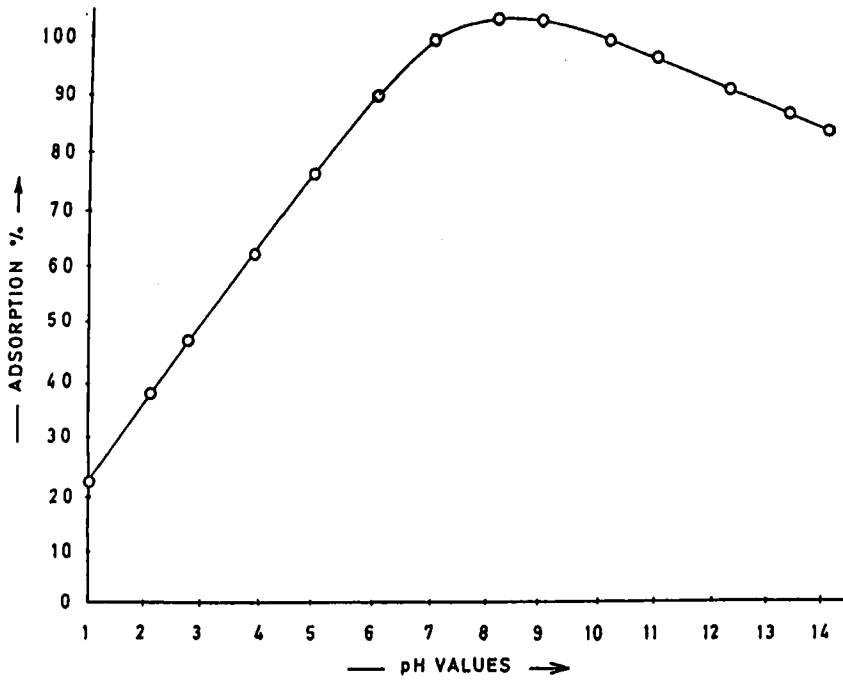
Figure 1   Per cent adsorption of chromium on MM as a function of pH.
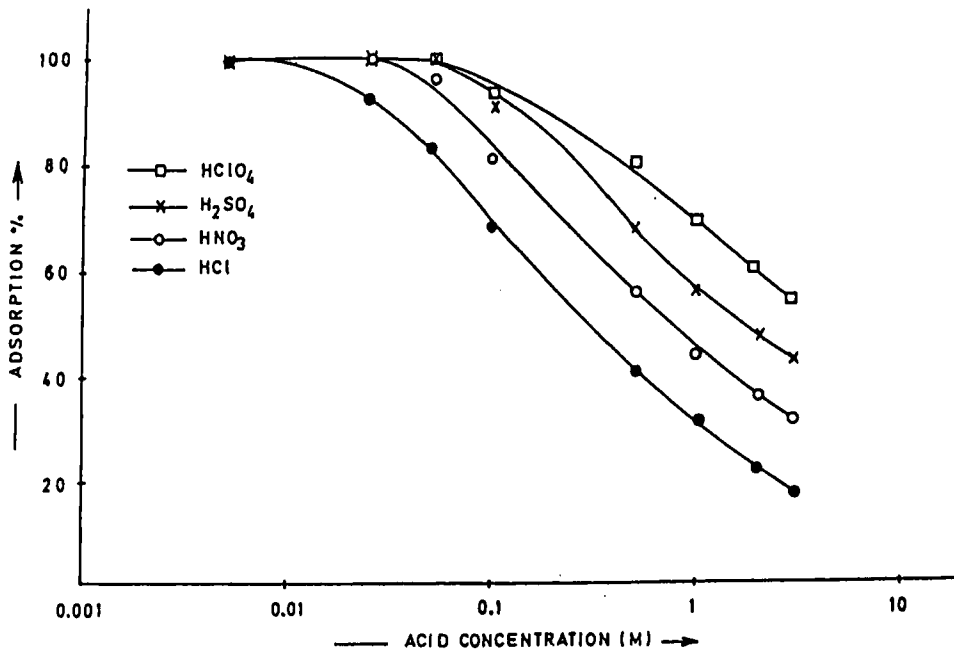

Figure 2   Per cent adsorption of chromium on MM as a function of acid concentration.

medium and positively charged hydrolysed species. Further, a higher acid concentration suppresses the hydrolysis of the elements, resulting in low adsorption.

A comparison of the adsorption from different acid solutions shows that there is no significant difference in adsorption behaviour of ^{51}Cr up to 0.01 M; however, at higher acid concentration the adsorption decreases in all the acids at a different rate. The decrease in HCl is more pronounced than in the other acids. This is advantageous, because liquid waste can have different compositions which may well change upon mixing with other effluent streams. Maximum adsorption was observed from 0.01 M HNO_3 and $HClO_4$ solutions; therefore, other parameters controlling the adsorption have been investigated using these solutions.

The dependence of the sorption of Cr on the amount of MM was studied in the range 10 mg–5 g using a 0.2% CrO_2 solution in 0.01 M HNO_3 (Figure 3). The per cent adsorption increases with an increasing amount of adsorbent and reaches a maximum of 98% from 300–500 mg. Therefore, all subsequent experiments were carried out with 500 mg of MM.

For the determination of the optimum contact time between the solid and liquid phases, the equilibration time was varied from 30 sec to 10 min. Figure 4 indicates that the sorption equilibrium between Cr and MM can be achieved within 6 min. Therefore, a 6 min contact time was employed in all subsequent measurements. The short equilibrium contact time shows that one is dealing with surface reaction. It is a hydrolytic adsorption, i.e. a simple condensation reaction between the hydrolysis
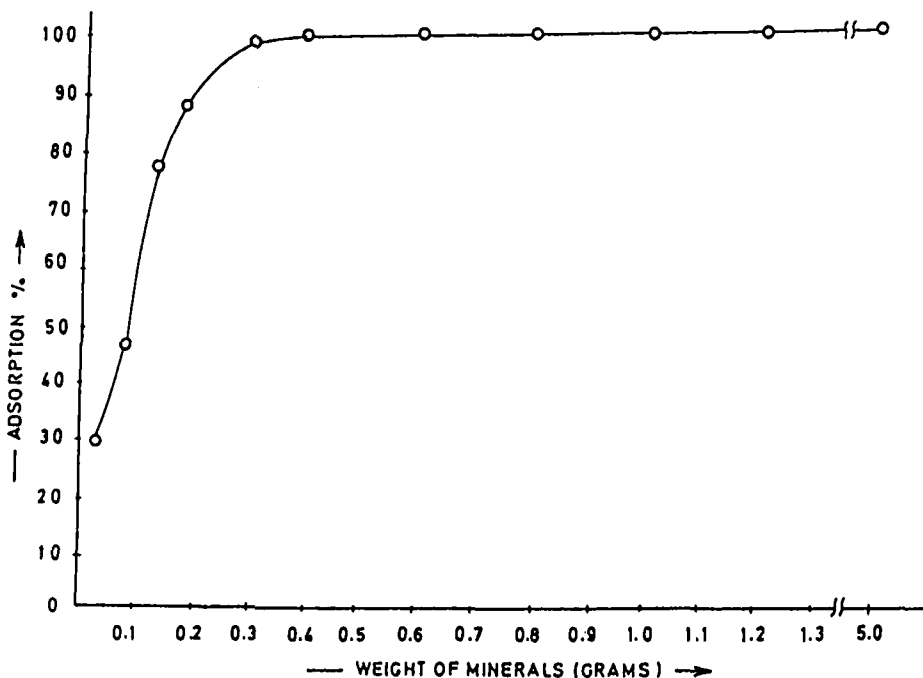

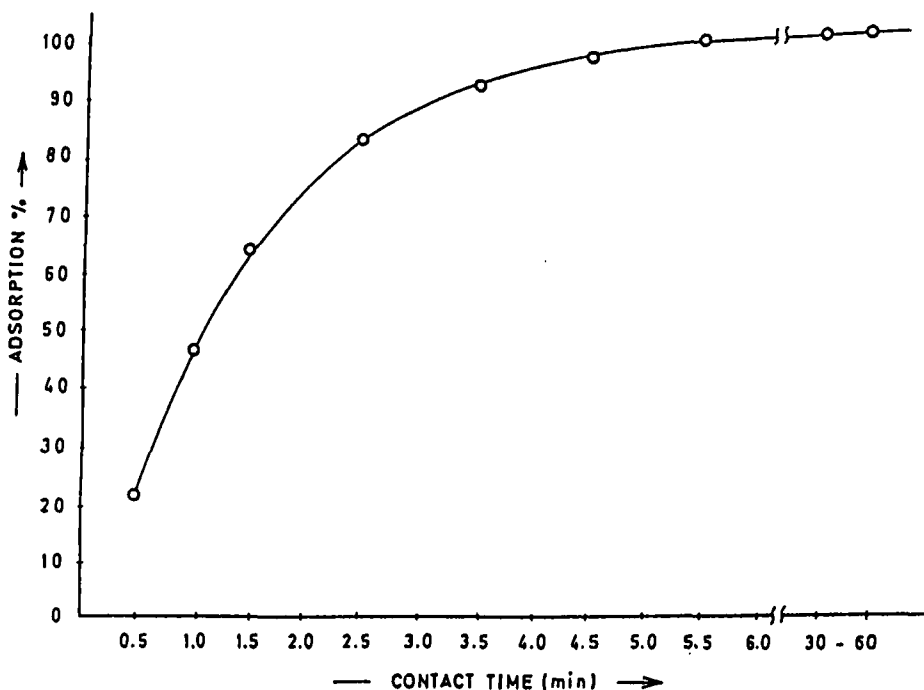Figure 3 Dependence of chromium adsorption on amount of sorbent (MM).

Figure 4   Per cent retention of chromium on MM as a function of contact time.

product of the metal ions and the sorbent carrying OH groups, with the formation of an oxygen bridge between Fe(III) minerals and chromium ions.[17,2,15]

Studies on the loading capacity of MM showed that up to 45 g Cr/kg sorbent can be retained under optimum conditions. Stirring or shaking has a relatively small influence on the rate and overall extent of adsorption. Several mineral mesh sizes were investigated; the results plotted in Figure 5 show that a fine grain size gives higher adsorption due to the availability of a larger area for adsorption.

The effect of temperature is shown in Figure 6. With increasing temperature the adsorption increases till 40°C and then start to decrease. The initial increase in adsorption may in part reflect the adsorption process to have a small activation energy. The decrease at higher temperature may be due to a change in elemental species. The results also show that a small change in temperature will only affect results by a few per cent.

The effect of additional anions on adsorption was studied using 0.01 M HNO_3 and $HClO_4$ acid solutions. Anions were added in the form of their sodium and potassium salts. All anions tested, including organic complexing anions did not interfere in the adsorption mechanism. The adsorption was also studied in the presence of a mixture of cations of different valency states added as their nitrates. Addition of a mixture of cations, particularly Cs, Sr, Hg, Eu, and Co, interfered in Cr adsorption on MM owing to the occupation by these cations of sites available
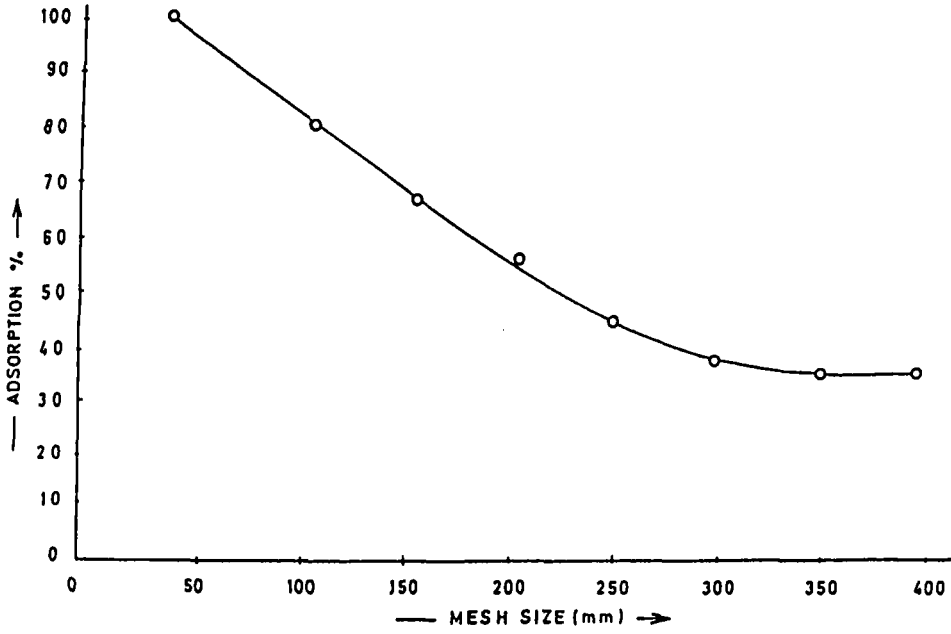
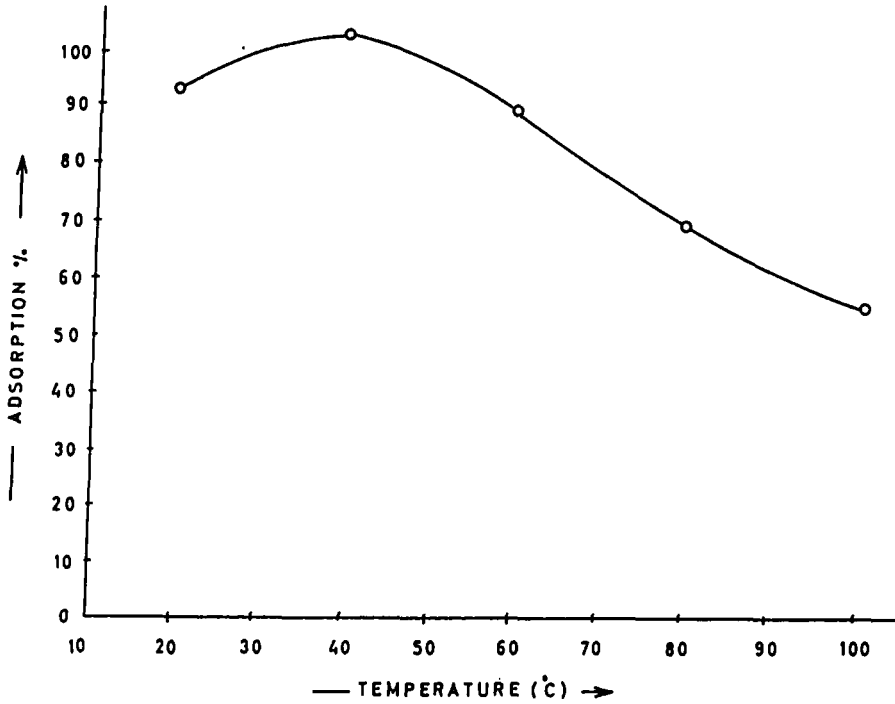**Figure 5**   Per cent adsorption of chromium on MM as a function of grain size.

Figure 6   Adsorption of chromium on MM as a function of temperature.

for adsorption on the adsorbent surface. Since effluents from tanneries and textile industries normally do not contain these (interfering) elements in high concentrations, this type of interference should be insignificant.

CONCLUSIONS

Decontamination of Cr can be achieved in less than 10 min over a wide range of pH values using MM sorbent, thus avoiding time-consuming pH adjustment. No expensive reagents are required as in, e.g. precipitation ion-exchange processes. Obviously, the untreated naturally occurring inexpensive mineral can be utilized effectively for the removal of chromium from industrial effluents by using a pond-type trap filter containing MM. A synthetic prefilter is necessary in front of the MM trap to stop the sludge and fibres which can block the trap and decrease the flow rate.

References

1. S. Music, *J. Radioanal. Nucl. Chem. Art.*, **100**, (1986), 185.
2. K. H. Lieser, In Separation and Filtration Method for Gas and Water Purification; (NATO Advance Study Institute Series, Noordhoff, Leyden, 1975.
3. B. Velte and A. Montiel, *J. Franc. Hydrol.*, **15**, (1984), 145.
4. Olin Chemicals, Hydrazine for Cr (VI) Reduction, Prospec No. 731–030, Stanford CT, U.S.A., 1981.
5. C. P. Huang and A. R. Bowers, *Progr. Water Techn.*, **12**, (1980), 629.
6. S. Ahmad and I. H. Qureshi, *J. Sep. Sci. Technol.*, **24**, (1989), 569.
7. B. R. Janes and R. J. Bartelett, *J. Environ, Qual.*, **12**, (1983), 169.
8. L. M. Mayers, L. L. Schick and C. A. Chang, *Geochim. Cosmochim. Acta*, **48**, (1984), 1717.
9. E. Nakayama, T. Kuwamoto, T. Fujinaga and H. Tokoro, *Nature*, **290**, (1981), 768.
10. S. Ahmad and D. F. C. Morris, *Min. Mag.*, **42**, (1978), 143.
11. S. Ahmad and D. F. C. Morris, *Analyst*, **103**, (1977), 17.
12. S. Ahmad and D. F. C. Morris, *Analyst*, **102**, (1977), 295.
13. J. Eakins, Symp. Atomic Energy Research Establishment, Harwell, U.K. (1967).
14. K. H. Lieser, *Radiochim. Acta*, **40**, (1986), 33.
15. J. A. Davis, R. O. Janes and J. O. Leckie, *J. Colloid Interface Sci.*, **63**, (1978), 480.
16. W. Faubel, *Radiochim. Acta*, **40**, (1986), 49.
17. S. Music, M. Gessener and R. H. H. Wolf, *J. Radioanal. Chem.*, **50**, (1979), 91.