PHYSICOCHEMICAL INVESTIGATION ON SORPTION BEHAVIOUR OF 51-CHROMIUM (VI) SPECIES AT METAL OXIDE - SOLUTION INTERFACE

by

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I N D I A

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Dedicated
to my
Parents

CERTIFICATE

This is to certify that the thesis entitled, **'PHYSICOCHEMICAL INVESTIGATION ON SORPTION BEHAVIOUR OF 51-CHROMIUM (VI) SPECIES AT METAL OXIDE-SOLUTION INTERFACE"** being submitted by Ms. RAMESH KUMARI to the Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by her. Ms. Ramesh has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis which, to my knowledge, has reached the requisite standard.

The results contained in this dissertation have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

Adsorption of metal ions on oxide surfaces is important from the point of view of analytical chemistry, environmental studies and disposal of radioactive wastes. The present investigation deals with the study of sorption behaviour of 51-chromium(VI) species on zirconium oxide, titanium oxide and bismuth oxide by radiotracer technique.

The effect of pH, concentration and temperature of adsorptive solution has been investigated under specified experimental conditions. The feasibility of sorption process has also been augmented with the influence of certain interfering/complexing ions. The experimental results are interpreted in the light of factors which control the change in the charge on the oxide surfaces as well as on the tracer chromate anion alongwith the subsequent interaction between adsorbate and adsorbent under prevailing experimental conditions.

The adsorption/desorption kinetics at varying concentrations (10^{-6}-10^{-2} M) and temperatures (303-323 K) of adsorptive solution show that both adsorption as well as desorption processes follow first order kinetics. Adsorption process has been found to be exothermic in nature and follows Freundlich adsorption isotherm over entire concentration range studied. The calculated thermodynamic parameters further confirms the spontaneity and exothermic nature of adsorption process and suggest some structural changes in the surface morphology.

The interfacial properties of these selected oxides have been characterised by their pH-metric titration curves, intrinsic dissociation constants (pK^{*}_{ai}) and zero point of charge (pHzpc) in varying concentration of KNO_3 and Na_2CrO_4 solution. The pHzpc values of all oxide samples have been observed to shift to a higher pH values in presence of $NaCrO_4$ solution and remain the same in presence of KNO_3 solution indicating specific adsorption for chromate ions. IR studies corroborates the existence of interactions between chromium(VI) species and oxide surfaces. Based on overall results a sorption mechanism on these oxides has been proposed in the light of Ligand-Exchange Mechanism.

A radioindicator study has also been attempted to examine the feasibility of concentrating microgram quantity of chromate ions from aqueous solutions under optimum experimental conditions. Thus, the sorption study is likely to find some useful applications for the concentration as well as minimising the environmental pollution of radioactive and inactive metals at trace level concentration.

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CHAPTER V

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