Abstract

The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in aquatic environment. Heavy metals have taken the center-stage due to their non-degradable, hazardous and toxic nature. The toxic metals, viz., As(III), Cd(II), Cr(VI), Co(II), Cu(II), Hg(II), Pb(II), Ni(II), Zn(II), etc., are found in the aquatic systems through wastewater from metal industries. Hence, the elimination of heavy metals from water and wastewater is of utmost importance to protect public health.

Adsorption process is promising in this regard as it achieves higher level of removal over a wider range of solution concentrations and generally reduce the quantity of solid residual that need to be disposed of. Activated carbons and synthetic resins have found ample use as adsorbent, however, the high cost of preparation and regeneration of activated carbon and synthetic resins prohibit their large-scale use in wastewater treatments. To overcome this problem, extensive studies have been done to find cheaper adsorbent materials. A large number of conventional and non-conventional adsorbents have been reported in literature, namely, bone charcoal, silica gel, natural and modified zeolites, natural and modified oxides, sawdust, rice husk, wheat bran, fly-ash, red mud, blast furnace slag and sludge, fertilizer waste slurry, peat, coal, chitin and chitosan, banana pith, waste tea leaves, orange peel, etc. The present work has been designed for using natural and modified clays as adsorbents with the following objectives:

(i) To prepare adsorbents from common clay minerals such as kaolinite and montmorillonite by calcination under controlled conditions,
(ii) To prepare other adsorbents from kaolinite and montmorillonite by intercalating with polyoxo and quaternary ammonium cations, and also by acid treatment,
(iii) To characterize the adsorbents with XRD, FTIR and to determine such properties as specific surface area, cation exchange capacity (CEC), etc.,
(iv) To use the adsorbents in batch processes for removing toxic metal cations from water by using synthetic effluents, and to evaluate the effects of various experimental conditions such as pH, concentration of metal ions, amount of adsorbent, etc., on adsorption capacity,
(v) To make a thorough study of the kinetics of adsorbate-adsorbent interactions in order to understand the mechanism of the interactions,
(vi) To test the validity and applicability of different adsorption isotherms to the adsorption equilibrium and hence to find out adsorption affinity and adsorption capacity of the natural and modified clays for the metal adsorbates, and
(vii) To determine the relevant thermodynamic parameters, $\Delta H$, $\Delta S$, $\Delta G$, for all the clay-metal interaction processes in order to examine spontaneity and other relevant characteristics that determine the suitability or otherwise of the adsorbents.

The thesis consists of five chapters and a bibliography.

The first chapter (Chapter 1: Introduction) outlines the objectives of the work undertaken. The chapter introduces clays and clay minerals with respect to their origin and occurrence, soil mineralogy, structural features, classification, important properties and general factors which control those properties, pillared and acid-activated clays, and the use of clay minerals in different fields. This chapter gives particular emphasis on the structure of kaolinite and montmorillonite. The important role played by the natural and modified clays in the environment with special emphasis on removal of heavy metals has been described based on literature survey. The scavenging capacity of clay minerals for organic and non-metallic inorganic pollutants from water has also been highlighted.

The second chapter (Chapter 2: Adsorption Technology: Theory and Practice) introduces the theoretical foundation of adsorption technology, which is the basis of the present work. Starting with a general definition of adsorption, the chapter deals with the historical development of adsorption, principles and factors influencing the extent of adsorption, different types of adsorption, and selectivity of an adsorbent. The chapter also describes different types of conventional and non-conventional adsorbents that have been used in laboratory as well as for industrial purposes reported in literature. The theories of adsorption equilibria have been discussed with special reference to the two most commonly used adsorption isotherms, namely, the Freundlich and the Langmuir isotherms. A detailed discussion of the adsorption kinetics in terms of Lagergren pseudo
first order equation, pseudo-second order equation, Elovich equation, and diffusion processes like intra-particle and liquid film diffusion has been given. The theoretical basis of thermodynamic study of adsorption processes is also included. The required mathematical equations of these models are incorporated along with the procedures to compute the parameters related to equilibrium, kinetics and thermodynamics studies. Brief description of different adsorption processes (Batch, Fixed bed and Moving bed process), desorption and regeneration of the adsorbent, etc., have also been included.

The third chapter (Chapter 3: Methodology and Adsorbent Characterization) outlines the experimental methodology used to arrive at the results. The chapter also includes the physico-chemical characterization of clays with respect to surface area (Sear’s method), cation exchange capacity (copper bisethylenediamine method), and confirmation of intercalation and modification of clays (XRD, FTIR spectroscopy).

The fourth chapter (Chapter 4: Adsorption of Toxic Metals) deals with the results of adsorption experiments done with Cd(II), Cr(VI), Co(II), Cu(II), Fe(III), Pb(II) and Ni(II) ions in aqueous solution with a number of clay adsorbents; namely, kaolinite, acid-activated kaolinite, ZrO-kaolinite, TBA-kaolinite, montmorillonite, acid-activated montmorillonite, ZrO-montmorillonite, and TBA-montmorillonite.

This chapter begins with a discussion of the role of metals in the environment. The toxic effects of the heavy metals (Cd, Cr, Co, Ca, Fe, Pb and Ni) with respect to their maximum permissible limit in drinking water, the minimal risk level recommended by the US-EPA, and the minimum exposure limit in workplace air as mandated by US-OSHA, are discussed.

The optimum conditions for use of the clay adsorbents have been investigated by carrying out the adsorption experiments under various controlled conditions. The pH has been shown to be a significant factor of influence on adsorption of the metal ions. Adsorption of Cd(II), Co(II), Cu(II), Fe(III), Pb(II) and Ni(II) could be carried out till the metal ions are precipitated as insoluble hydroxides. The pH at which precipitation commences is different for different metal ions and the effective pH-range for carrying
out adsorptive removal of the metals is also different for each. No such limitation is however observed for Cr(VI) as the metal exists in the form of anions and therefore, precipitation as hydroxide is not possible. The acid activated clays have higher adsorption capacities compared to the non-activated clay, whereas ZrO- and TBA-derivatives show lower degree of adsorption compared to their respective parent clays. The extent of adsorption (%) as well as the amount of metal ions adsorbed on unit mass of clay ($q_e$) shows increasing trends with pH until the precipitation begins. For Cr(VI), the extent of adsorption (%) and $q_e$ increases up to pH 7.0, after which they show a steady decrease.

The influence of time and kinetics of adsorption for metal removal have been elaborately reported. For all the metal-clay interactions, both the extent of adsorption (%) and the amount of metal ions adsorbed on unit mass of adsorbents ($q_t$) increase if the interaction is carried out for longer time interval. The equilibrium time varies from metal to metal (Cd(II): 240 min, Cr(VI): 240 min, Co(II): 240 min, Cu(II): 360 min, Fe(III): 300 min, Pb(II): 180 min, and Ni(II): 180 min). The kinetics of clay-metal interactions are studied with different models, namely, Lagergren first order kinetics, second order kinetics, Elovich equation, intra-particle diffusion and liquid film diffusion. The second order mechanism has been found to be more appropriate in describing the kinetics in most cases. The second order kinetics indicates that the metal ions and the substrate atoms (on clay surface) both participate in the rate processes. However, for Cr(VI)-clay interactions, it is interesting to note that, non-activated kaolinite and acid-activated kaolinite are more likely to take up Cr(VI) with a first order mechanism while ZrO-kaolinite and TBA-kaolinite may follow second order mechanism. The formation of chemisorptive bonds between metal ions and clay adsorbent are confirmed by the application of Elovich equation. The non-zero intercepts obtained from the intra-particle diffusion plots for the interactions show relative incompatibility of this model to the present study. However, the applicability of the liquid film diffusion model shows a distinct possibility in several cases in this work. Thus, in most cases, diffusion from the bulk liquid phase to the surface of the adsorbent is likely to control the kinetics of the adsorption process.
The extent of adsorption (%) increases rapidly when the adsorbent amount is increased. However, the corresponding amount of metal ions adsorbed per unit mass ($q_e$) decreases for all the clay adsorbents. Acid activated kaolinite or montmorillonite has a higher adsorption capacity compared to the non-activated clays and the acid-activated montmorillonite has the highest adsorption capacity among all the clay adsorbents. The removal of metal ions on ZrO- and TBA-clays is lower than their parent clays.

When the initial adsorbate concentration is increased the extent of adsorption (%) shows a decrease. The increase in metal ion loading has a positive impact on the amount adsorbed per unit mass ($q_e$). Again, the acid-activated montmorillonite has the highest adsorption capacity, while the uptake of metal ions on ZrO- and TBA-clays is lower than the non-activated clays.

The clay-metal interaction data have been fitted in each case to Freundlich and Langmuir adsorption isotherms. Langmuir model has been found to be more suitable to describe the adsorption equilibria in all the cases. Large values of equilibrium coefficient, $b$, ensure that the equilibrium is predominantly driven towards the formation of the adsorbate-adsorbent complex. The value of Langmuir monolayer capacity, $q_m$, is highest for acid-activated montmorillonite. It is suggested that the treatment with acid does not increase the number of adsorption sites to a large extent but the treatment influences the strength of the existing sites. Introduction of ZrO- and TBA- reduces the number of available adsorption sites for metal ions and consequently $q_m$ for ZrO- and TBA-derivatives is smaller than that for the parent kaolinite and montmorillonite.

The thermodynamics of adsorption for Pb(II), Ni(II), Fe(III) on all the eight clays and Co(II) on montmorillonite has shown an exothermic process with adsorption decreasing with increasing temperature. The adsorbate ions have a tendency to leave the solid phase to the bulk solution with the rise in temperature. However, the adsorption of Cr(VI), Cd(II), Cu(II) on all the eight clays and Co(II) on kaolinites is endothermic in nature and a small activation energy is required for overcoming an energy barrier before the adsorptive could be attached to the surface. In all the cases, the thermodynamic
parameters of enthalpy, entropy and Gibbs energy are computed and the values agree with those of a spontaneous process.

The fifth chapter (Chapter 5: Conclusion) summarizes the conclusions drawn from the experimental work and outlines a few suggestions for further work.

The thesis gives a complete list of all the references, which have been consulted during the work.