ABSTRACT OF THE Ph.D. THESIS

The thesis presents systematic investigation of adsorption isotherms, adsorption kinetics, diffusion mechanism and adsorption thermodynamics of prepared activated carbon from the wood apple shell. The activated carbon was prepared by chemical, combined chemical and physical activation method. The prepared activated carbon was characterized by SEM, X-ray diffraction, FTIR and pH at point of zero charge methods. The activated carbon was used for the removal of metal ions such as Cr (VI), Pb (II) and Cd (II) and organic dyes such as Methylene blue, Crystal violet and Congo red from aqueous media. The prepared activated carbon have been used as an effective adsorbent. The thesis has been organized as follows:

Chapter 1 provided the introduction and theoretical consideration of adsorption concept including the adsorbate, adsorbent surface and textural properties. It also summarizes the commonly used adsorption isotherms, adsorption kinetics, intra-particle diffusion and adsorption thermodynamic with detail mathematical equations. Chapter 2 deals with the literature review with respect to the various low cost materials or activated carbon prepared from the agricultural waste material. The first main aim of literature review was to know the adsorption capacity of studied toxic metals and dyes from wide range of prepared carbons and precursors. The widely used adsorption isotherms like Langmuir and Freundlich isotherm along with their parameters were reviewed and adsorption capacity were compared and discussed. Secondly, adsorption dynamics along with the diffusion mechanism was reviewed and discussed. Finally, review shows the significance of thermodynamic parameters, standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) to predict the spontaneity of adsorption of metals, dyes and other organic pollutant onto the surface of different adsorbents.

Chapter 3 deals with the study of hexavalent chromium adsorption capacity of powdered wood apple shell (Limonia acidissima L.). The well-known adsorption kinetic, thermodynamic parameters and adsorption isotherm studies have been reported to interpret the adsorption behaviors at different temperature. In addition to the effect of temperature, effects of pH and metal concentration on percentage of sorption have also been investigated. Powdered wood apple shell was characterized by SEM, FTIR and pH at zero point charge method. Chapter 4 comprises the Cr (VI) adsorption capacity of activated carbon prepared from wood apple shell by both chemical and physical activation methods. Activated carbon
material was synthesized from wood apple shells using H\textsubscript{2}SO\textsubscript{4} as chemical activating agent and further activated by physical activation method in muffle furnace ambient atmosphere at 600°C. The carbon material obtained was used as adsorbent for the removal of Cr (VI) metal ion. The activated carbon material was characterized by powder X-ray diffraction, Scanning Electron Microscopy, pH at zero point charge and FTIR methods. The presence of numerous sharp distinct peaks is suggestive of the crystalline nature of activated carbon, indicating that the prepared activated carbon in the present system was crystalline graphite. This double activation method was very effective for developing the wide range of pores with different sizes and shapes on surface of activated carbon and hence leading to large surface area activated carbon. The adsorption study investigated the removal of toxic Cr (VI) metal ions from aqueous solution onto the surface of activated carbon derived from wood apple shell. The well-known adsorption isotherms such as Langmuir, Freundlich, Dubinin–Radushkevich and Flory-Huggins were investigated and analyzed. The Langmuir monolayer adsorption capacity of Cr (VI) onto prepared activated carbon was 151.51 mg g\textsuperscript{-1} at 300 K. The Pseudo-first and Pseudo-second order adsorption kinetic was studied and it revealed that the pseudo-second order model fitted very well to the adsorption of Cr (VI) on activated carbon indicating that the adsorption process follows chemisorptions. Intra-particle diffusion model analysis suggests that adsorption of Cr (VI) onto activated carbon was controlled by both film as well as pore diffusion mechanism. The investigation shows that the agricultural waste biomass wood apple shell can be effectively utilized for preparation of activated carbon and become a promising adsorbent for the removal of Cr (VI) from aqueous solutions.

Chapter 5 presents the comparative adsorption capacity, adsorption kinetics and the diffusion mechanism of Cd (II) and Pb (II) metal ions onto activated carbon prepared from wood apple shell by chemical and physical activation methods. The well-known adsorption isotherms such as Langmuir and Freundlich were investigated and analyzed. Equilibrium data were well described by the Langmuir and Freundlich isotherm, suggesting the monolayer adsorption as well as the heterogeneous nature of activated carbon for the adsorptions of Cd (II) and Pb (II) ions. The Pseudo-first, Pseudo-second order and Elovich kinetic was studied which reveals that the pseudo–second order model fitted very well to the adsorption of Cd (II) and Pb (II) ions on activated carbon and further confirmed the chemisorptions by Elovich kinetic model. Intra-particle diffusion model analysis suggests that adsorption of Cd (II) and
Pb (II) ions onto activated carbon was controlled by both film as well as pore diffusion mechanism.

Chapter 6 deals with efficiency of activated carbon produced from wood apple fruit shell powder by ZnCl\(_2\) activation for the removal of Crystal violet and Congo red dye. Chemical activation by ZnCl\(_2\) improves the pore development in the carbon structure, and the yields of carbon are usually high. The prepared activated carbon was characterized by SEM, XRD and pH at zero point charge (pH\(_{pzc}\)) method. X-Ray diffraction analysis has been used to analyze crystalline and amorphous nature of the prepared activated carbon. The efficient pores activated carbon was prepared by zinc chloride activation method and well characterized by XRD and SEM analysis. The ability of zinc chloride activated carbon was investigated for the removal of Crystal violet and Congo red dyes in aqueous solutions. Equilibrium data was well evaluated by the Langmuir, Freundlich and Temkin isotherms, suggesting Freundlich isotherm fits very well as the heterogeneous nature of zinc chloride activated carbon for the adsorptions of Crystal violet and Congo red dyes. Batch adsorption kinetic studies showed that, the adsorption of dyes followed pseudo-second order kinetics and at four different concentrations studied, indicating chemisorptions is the rate-limiting step. The thermodynamic study revealed that the removal of dyes from aqueous solution onto zinc chloride activated carbon was spontaneous, feasible and endothermic process at temperature greater than standard equilibrium temperature. The investigations reveal that the zinc chloride activated carbon is a promising adsorbent for removal of dyes from contaminated wastewater.

Chapter 7 summarizes the methylene blue adsorption capacity of prepared activated carbon. The activated carbon was prepared by H\(_2\)SO\(_4\) chemical activation along with microwave activation method from wood apple shell. The common Langmuir and Freundlich adsorption isotherms and kinetics of methylene blue adsorption on the prepared activated carbon were analyzed. The prepared sulfuric acid activated carbon was characterized by SEM, XRD and FTIR analysis method. Adsorption dynamics analysis indicates that pseudo-second order equation fitted very well to the adsorption of MB on sulfuric acid activated carbon. Adsorption system is not totally controlled by intra-particle diffusion mechanism. The Elovich kinetic model confirms chemisorptions mechanism. The adsorption process fits the Langmuir isotherm model better than Freundlich isotherm. These results suggest that microwave oven activated charcoal prepared from wood apple shell is a potential adsorbent
for the dye removal from industrial wastewater. Chapter 8 summarizes the overall adsorption capacity of prepared activated carbon from wood apple shell of heavy metal ions (Cr (VI), Cd (II) and Pb (II)) and dyes (Methylene blue, Crystal violet and Congo red) from aqueous solutions. Further it also deals the future scope of prepared activated carbon in environmental and other applications.

LIST OF PUBLICATIONS BASED ON THE RESEARCH WORK

Refereed International Journals


Presentations in Conferences

1. **Kailas M. Doke***, Ejazuddin M. Khan¹, Mujahid Yusufi¹, Joseph Rapolu², Effect of pH and temperature on the biosorption of hexavalent chromium onto wood apple shell; Equilibrium, kinetic and thermodynamic studies, National Conference on Environmental Innovations for Resource Sustainability held at School of Environmental and Earth Sciences, North Maharashtra University, Jalgoan, Maharashtra (21st to 22nd January 2011).