Studies on Natural Adsorbents for THE ISOLATION of Industrial Pollutants from Waste water Samples around Delhi

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The discharge of coloured wastewater from paper and pulp, textile and dyeing, leather, printing industries, and industrial effluents containing toxic metals including Cd(II), Pb(II) and Cr(VI) from electroplating, batteries and paints industries is currently a major environmental concern in the developing countries because of their poor bio-degradability, carcinogenicity and toxicity. Consequently, the removal of such pollutants from aqueous effluents is of significant environmental, technical and commercial importance. Different process for removal of dye or toxic metals from industrial wastewaters has been reported in the past. Over the years, the adsorption process has emerged as a viable and effective alternative to most of these conventional treatment techniques, which are rather expensive. A large number of low-cost adsorbents have been utilized for the removal studies of dyes as well as metal ions, and the search for more cheaper and effective adsorbents still continues unabated.

In the present work, we have carried out the adsorption studies of some basic dyes, namely, methylene blue, malachite green and rhodamine B; and the toxic metal ions, cadmium(II), lead(II) and chromium(VI) onto some naturally occurring and low-cost adsorbents viz.; coal (Akash Kinari) and soil (clayey) and the utilization of fly ash as adsorbent has also been studied for the removal of these dyes and metal ions.

The composition of the coal sample indicates that carbon (47.11 %), silica (61.11 %), and alumina (22.57 %) are its major chemical constituents. The composition of the present Akash Kinari coal is different from those previously studied. The porosity (0.43), surface area (12.34 m^2/g), mean particle diameters (49 x 10^{-2} cm) and density (3.31 g/cm^3) of the coal sample have been determined. The adsorbent has been further characterized by the FT-IR spectrum, X-Ray diffraction and Scanning Electron microscopic studies. The IR spectrum (4000-500 cm^{-1}) of the coal displays adsorption bands indicative of the presence of carboxylic, phenolic and alcoholic groups. The prominent d-lines in the X-ray diffractogram of the adsorbent are in good agreement with the characteristic diffraction patterns of kaolinite, haematite and quartz, while its scanning electron micrograph shows structural features with non-uniform size and surface.

The removal of three dyes, methylene blue, malachite green and rhodamine B from aqueous solutions at different concentrations, pH and temperatures by Akash Kinari coal has been studied. It has been found that per cent adsorptions of methylene blue, malachite green and rhodamine B onto the adsorbate decrease from 97.18 to 83.90,

89.16 to 79.77 and 78.40 to 67.35, respectively, when their concentrations in solutions are increased from 5 to 20 mg/L at 30± 1 ° C at pH 6.8, 7.2 and 5.8, respectively. The rate constants of adsorption (K_{ad}) for methylene blue, malachite green and rhodamine B are found to vary between 4.27–3.95 x 10^{-2}, 4.53–4.61 x 10^{-2}, and 4.39–4.20 x 10^{-2} /min at 20, 30, and 40 ° C, respectively. The observed data on the adsorption of dyes at different temperatures fits well the Langmuir isotherm model. The calculated values of the Langmuir constant for adsorption capacity of the dyes (Q^o) on the adsorbent at different temperatures vary from 2.12 to 1.59, 2.68 to 1.15 and 1.23 to 0.78 mg/g. The magnitude of equilibrium parameters, R_L lies between zero and one indicating a favourable adsorption process. The equilibrium data at different dye concentrations are fitted with Freundlich isotherm model and the values of Freundlich constants, n and $K_F$have been evalulated. The values of n and K_F between zero and one indicate the favourable adsorption of dyes on the coal. There is an increase in the adsorption of methylene blue, malachite green and rhodamine B from 74.39 to 92.80 per cent, 62.16 to 83.42 per cent, and 51.57 to 71.78 per cent, respectively (at 30±1 ° C and 10 mg/L concentration) with increase in pH from 3.8 to 7.2. The adsorption of dyes, however, decreases beyond pH 7.2. Various thermodynamic parameters (D G° , D H° and D S°) have also been calculated. The negative values of D G° indicate that the adsorption of dyes onto coal is a spontaneous process. The values of D H° are also negative which confirms that the process is exothermic. The negative values of D *S*°suggest the probability of favourable adsorption.

Adsorption of Cd(II), Pb(II) and Cr(VI) metal ions onto coal from aqueous solutions have been studied as a function of contact time, temperature, concentration and pH. The adsorption of metals increases from 78.92 to 87.66 per cent when the concentration of Cd(II) is decreased from 2.0 to 1.0 mg/L; from 72.31 to 89.14 per cent with decrease in concentration of Pb(II) from 6.0 to 2.0 mg/L, and from 81.90 to 90.40 per cent, when the concentration of Cr(VI) is decreased from 20.0 to 5.0 mg/L at 30 ° C at pH 8.5, 6.5 and 2.0, respectively. The adsorption isotherms and kinetics of adsorption have been studied at different temperatures. The rate constants of adsorption (K_{ad}), calculated using Lagergren rate equation, for Cd(II), Pb(II) (at 2 .0 mg/L concentration) and Cr(VI) (5 .0 mg/L concentration) vary between 4.28 – 6.18 x 10^{-2} , 4.82 – 6.67 x 10^{-2} , and 3.55 – 4.20 x 10^{-2} /min at 20, 30, and 40 ° C, respectively. The applicability of Lagergrens' equation suggests a first-order kinetics for the uptake of metal ions. The linear plots of C_e/q_e vs. C_e at different temperatures, and close to unity values of the correlation coefficients, r^2, obtained from these linear plots, indicate the applicability of Langmuir adsorption isotherms. The values of Langmuir constants, Q° and b have been calculated. The values of R_l are between zero and one indicating favourable sorption. The linearity of the plots of log q_e vs. log C_e and close to unity values of r^2 and 1/n indicate that the Freeundlich isotherm is also applicable. The per cent uptake of Cd(II) increases from 57.80 to 85.66, Pb(II) from 72.11 to 94.01, and Cr(VI) from 84.36 to 94.78 with rise in temperature from 20 to 40 ° C at pH 8.5, 6.5 and 2.0, respectively, for 2.0 mg/L initial concentrations of Cd(II) and Pb(II), and 3.0 mg/L of Cr(VI). The values of

D G° are negative, while that of D H° and D S° are positive, which indicate that the sorption process is spontaneous and endothermic. The extent of adsorption of Cd(II), Pb(II) and Cr(VI) at different pH at 30 ° C has been studied. The maximum adsorption of Cd(II) occurs at pH 8.5, of Pb(II) at 6.5, and that of Cr(VI) at pH 2.0. The results show that the coal is a good adsorbent for the removal of dyes and metal ions from the industrial effluents.

The important chemical constituents (per cent) of the fly ash are: SiO_2, 60.10; Al_2O_3, 18.60; Fe_2O_3, 6.40; CaO, 6.30; MgO, 3.60, which indicate that silica and alumina are the major constituent. The surface area, 40.16 m^2/g; porosity, 0.43; bulk density, 3.51 g/cm^3; and ignition loss, 4.90 of the sample has been determined. The adsorbent is characterized by FT-IR spectrum, X-Ray diffraction and scanning electron microscopy. The FT-IR spectrum in the range 4000-4000 cm^{-1} region displays weak and broad adsorption bands in the range 3890-555 cm^{-1}. These bands may reasonably be attributed to the presence of carbonyl, carboxyl, lactones, phenols, amines and imines and hydroxyl groups. The X-ray diffractogram of the fly ash shows several peaks, which are indicative of the presence of quartz, kaolinite, illite, calcite, hematite and magnetite. The scanning electron micrograph at 100 x and 1000 x magnifications of the adsorbent (75 µm mesh size) shows typical fly ash morphology and surface texture. The adsorbent consists mainly of solid spheres of a wide range of sizes. The bigger particles are made up of the aggregates of smaller particles.

Fly ash has been utilized as a potential low-cost adsorbent for the removal of methylene blue, malachite green and rhodamine B from artificial textile wastewater. Adsorption of these dyestuffs has been studied in terms of various processes factors such as initial concentration, pH, and temperature and contact time. The results indicate that overall percent removal of methylene blue, malachite green and rhodamine B vary between 73 to 93, 46 to 89 and 54 to 77, respectively. The removal of dyes increases with increase in contact time and the pH from 3 to 10, and decreases with increase in the initial concentration of the dyes from 5 to 20 mg/L. Both Langmuir and Freundlich isotherm models have been employed to evaluate the experimental data. The equilibrium data has been found to fit both Langmuir and Freundlich isotherms, but Freundlich isotherm fits the data better. The calculated values of the changes in standard free energy (DG°), standard entropy (DS°) and standard enthalpy (DH°) indicate that the adsorption process is favourable, physical and exothermic. The adsorption capacity of the adsorbent increases with decreasing particle sizes.

The extent of adsorption of Cd(II), Pb(II) and Cr(VI) ions onto fly ash increases rapidly in initial stages but becomes slower in the later stages till saturation. The percentage removal of Cd(II) at pH 8.5, Pb(II) at pH 6.5 and Cr(VI) at pH 2.0 decreases with increase in the initial concentration of the metal ions. The adsorption data best fit the first-order kinetics equation. The K_{ad}values at different concentrations have been calculated from the slopes of the linear plots of log (q_e-q) vs. t. The experimental data at different

temperature follows the rearranged Langmuir adsorption isotherm. The applicability of Langmuir isotherm suggests the formation of monolayer coverage of the adsorbates on the surface of the fly ash. The dimensionless factor, R_L are between zero and one thereby indicating favourable adsorption. The decrease in the values of Q° with increase in temperature indicate the exothermic nature of the sorption process for both Cd(II) and Pb(II), while for Cr(VI) the Q° values increases as the solution temperature is raised from 20 to 40 ° C, indicating the process to be endothermic in nature. The adsorption data fits well the Freundlich adsorption isotherm and the values of the Freundlich constants are calculated. The negative values of DH° for Cd(II) and Pb(II) suggest the exothermic sorption, whereas positive values of DH° indicates the endothermic nature of Cr(VI) removal. The results of sorption studies at different pH values between 2 to 10 have been discussed on the basis of competitive adsorption of H^+ and OH^- with the adsorbates. The results show that the fly ash is a good adsorbent for the removal of dyes and metal ions from the textile, and electroplating wastewaters.

The clayey soil is used as a potential low-cost natural adsorbent for the removal of methylene blue, malachite green and rhodamine B from the artificial textile wastewater. The chemical composition (%) of the sorbent sample is found to be: SiO_2, 44.21; Al_2O_3, 40.72; Fe_2O_3, 0.53; MgO, 0.12; Na_2O, 0.014; K_2O, 0.27; P_2O_5, 0.032. The density, porosity and surface area are found to be 2.57 g/cm^3, 0.39 % fraction and 12.7 m^2/g^2, respectively. The adsorbent has been characterized by FT-IR spectrum, X-ray diffraction and scanning electron microscopy. The FT-IR spectrum in the 4000-500 cm^{-1} region displays weak and broad bands between 3922-517 cm^{-1} attributed to the presence of carboxyl, carbonyl, lactones, amides, esters, imines and aromatic compounds. The absorption bands due to Fe-O, Mg-O, and Si-O-Al linkages are present in the spectrum. The d-lines corresponding to the presence of Al_2O_3, SiO_2, Fe_2O_3 and MgO are observed at their appropriate places. The diffractrogram reveals the presence of quartz, calcite, goethite, silicate, fluorite, hematite and gypsum.

Adsorption of these dyestuffs on soil as natural adsorbent has been studied in terms of the processes factors such as initial concentration, pH, and temperature, particle size and contact time. The overall percent removal of methylene blue, malachite green and rhodamine B decreases from 89.18 to 76.80, from 83.20 to 61.70 and 71.56 to 57.30, respectively, with increase in dyes concentration from 5 to 20 mg/L. The rate constants, calculated by employing the Lagergren rate equation, indicate the first-order nature of the sorption process. The adsorption of dyes is found to increase with increase in temperature from 20 to 40 ^oC, which indicate that the process is endothermic. The increase in adsorption with rise in temperature has been explained in terms of various thermodynamic parameters. The equilibrium data fits both Langmuir and Freundlich isotherms. The values of Q^o increase with increase in temperature, thereby confirming the process to be endothermic. The effect of pH on the adsorption capacity of the adsorbent has also been studied. The removal of dyes increases with the decrease of the

particle size of the soil.

Sorption of metal ions is found to be dependent on the contact time, temperature, concentration, adsorbent dose and pH of the solution. The adsorption of metal ions (in percent) decreases from 92.12 to 86.14 when concentration of cadmium ions increases from 1.00 to 2.00 mg/L, and from 94.40 to 90.66 when concentration of Pb(II) ions increases from 2.00 to 6.00 mg/L, and from 96.80 to 89.92 when concentration of Cr(VI) ions increases from 5.00 to 20.00 mg/L. The values of the correlation coefficients, r^2 show that both the Langmuir and Freundlich models adequately describe the adsorption data. The Langmuir and Freundlich constants have been calculated. The values of R_L are found to be less than unity, indicating a favourable adsorption process. The rate constants of adsorption (K_{ad}, 10^{-2} / min) for Cd(II), Pb(II) for 2.0 mg/L concentration and Cr(VI) for 5.0 mg/L concentration varies between 3.02 to 3.55; 4.84 to 3.98 and 3.59 to 5.05 at 20, 30 and 40 ° C, respectively. The thermodynamic parameters (D G° , D H° and D S°) have also been calculated. The negative values of D G° for Cd(II), Pb(II) and Cr(VI) indicate the feasibility and spontaneous nature of the process. The values of D H° are found to be positive which suggest the endothermic nature of adsorption. The positive values of D S° show the increased randomness at the solid-solution interface with some structural changes in the adsorbate and adsorbent and an affinity of the adsorbent toward metal ions. The adsorption of metal ions has been examined from solutions over a pH range from 2 to 9. The optimum adsorption of Pb(II) is observed at pH 6.0 for an initial concentration of 2.0 mg/L. The percentage adsorption of Cd(II) increases as the pH of the solution is increased and reaches to a maximum value at pH 9. The results of the effect of pH on Cr(VI) removal by soil are in agreement with those reported by other investigators. The overall data shows that the soil is a good adsorbent for the removal of dyes as well as metal ions from the industrial effluents from the textile, electroplating and other metal finishing and allied industries, and inks, paints, pigments, leather tanning industries.

The results and conclusions that flow from these studies add a new perspective to our understanding of this broad and fascinating field. However, the search for low-cost, effective and alternative adsorbents for the removal of industrial pollutants will continue and much further researches in the area is needed.