Application of Mentha Plant Ash derived from distilled *Mentha piperita* plant waste as adsorbent in removal of dyes and heavy metals from aqueous solutions

SUMMARY
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Summary

The present investigation covers the potential application of Mentha Plant Ash (MPA) derived from distilled mentha plant waste as an efficient adsorbent in removal of basic cationic dyes (MG and MB) and Cr(VI) from their aqueous solutions. Mentha (mint) Plant Ash, a dumping waste was collected from local mentha oil distillation units, Barabanki, Uttar Pradesh, India. Prior to use, MPA was homogenized to a fine powder and the resulting powder was sieved (< 0.21 mm) by using 70-mesh size sieve so that all the particles were of almost of uniform size. The various physico-chemical characteristics of MPA as an adsorbent were determined using Zeta Potential Analyzer, Scanning Electron Microscope (SEM), Energy dispersive X-Ray Spectroscopy (EDX), X-Ray Photoelectron Spectroscopy (XPS), Brunauer-Emmett-Teller (BET), Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), Thermo gravimetric Analyzer (TGA) and Cyclic Voltammetry. BET specific surface area, total pore volume and average pore diameter of MPA particles were also analyzed. Presence of low boiling volatile organic matter, moisture content, hemicellulose, cellulose and lignin in the MPA adsorbent were confirmed by Thermo-gravimetric analysis (TGA) and various surface functional groups by IR-Spectroscopy (FTIR). The IR-spectra of MPA exhibit that hydroxyl, ester, amine, phenyl, carboxyl and carbonyl groups are the surface functional moieties, not only contributing to negative charge on surface of adsorbent, but may be actively involved in the binding of cationic dyes and Cr(VI) metal ions. The value of zeta potential of MPA particles at neutral pH (pH 7.0) was determined as −37.1 mV, indicating a highly negatively charged sorption surface of MPA particles. A highly electronegative surface along with

little effect of changing pH condition on the zeta potential suggested about larger contribution of salts and minerals in determining the zeta potential of adsorbent (MPA). This could be the reason for high binding efficiency of MPA for cationic dyes (MG and MB) and Cr(VI) metal ions. The shape of the N_2 adsorption/desorption isotherm matches the Type IV shape of adsorption isotherm (IUPAC classification), indicating a mesoporous structure of MPA particles. The characteristics of Type IV isotherm correspond with monolayer-multilayer adsorption and are indicative of relatively strong interaction between adsorbent surface and adsorbate molecules. The BET specific surface area of MPA was found to be 7.169 $m^2 g^{-1}$. A pore diameter in MPA particles between 2 to 50 nm indicates a mesoporous material. The presence of clay minerals such as calcite, quartz, sylvite and dolomite were confirmed in the XRD pattern of MPA. SEM image of MPA showed irregular surface with heterogeneous pore structures on the surface of MPA particles. The EDX analysis of the MPA exhibited chemically rough surface of MPA particles was due to major contribution of Mg, Cl, K, Si, Fe, Ca C, O and Al content. The cyclic voltammetry analysis of cationic dyes (MG and MB) and Cr(VI) showed a reversible, coupled redox reaction at the interface of dye/metal ions and MPA particles. Further, the Cr 2p peaks in the binding energy range (0 – 1200 eV) and (570 – 595 eV) were analyzed in recorded XPS spectrum of MPA after adsorption of Cr(VI). The binding energy in the range of 572–581 eV and 582–591 eV corresponds to Cr 2p3/2 and Cr 2p1/2 orbitals, respectively. The binding energy (eV) peaks of Cr $2p_{3/2}$ and Cr $2p_{1/2}$ were detected at around 579.2, 588.8, 577.6, 588.0, 576.8 and 585.6 eV in the recorded XPS spectrums and these peaks were assigned to Cr(VI), Cr(III) and Cr(II) forms.

Adsorption behavior of MPA in removal of basic cationic dyes (MG and MB) from aqueous solutions was analyzed as a function of different pH (4.0 – 10.0), initial dye concentration (20 – 100 mg/L for MG and 5 – 50 mg/L for MB), contact time (0 – 45 min for MG; 0 – 30 min for MB), dose of adsorbent (0.05 – 0.3 g/100 mL of MPA) and temperature (20 – 50°C). Similarly, the sorption of Cr(VI) by MPA was carried out as a function of different contact time (0 – 90 min), adsorbent dose (0.1 – 0.5g/100 mL), pH condition (3 – 9) and initial Cr(VI) concentration (10 – 50 mg L^{-1}) to define the optimum conditions for the adsorption of Cr(VI). The MG and MB dye removal by MPA initially occurred at a faster rate, corresponding to 72.86 and 74.68 % removal within 5 min, respectively. Similarly, the adsorption of Cr(VI) at different metal ion concentration by MPA showed initially a rapid sorption process up to 30 min, followed by slowing down of the sorption process with increase in the contact time up to 90 min. A rapid rate of initial dye/heavy metal removal by MPA could be due to maximum availability of vacant binding sites on the surface of adsorbent, ensuring high efficiency of dye/heavy metal removal. The maximum MG and MB dye removal, at an adsorbent dose of 0.1 g/100 mL, was found to be 36.86 and 20.65 mg g^{-1}, respectively. A rapid phase of dose-dependent increase in Cr(VI) metal ion removal was found to occur up to 0.2 g/100 mL dose of MPA and this was followed by a sluggish phase of Cr(VI) removal between 0.2 to 0.5 g/100 mL of dose of adsorbent. In the present study, the biphasic pattern of dose dependent dye/heavy metal removal could be interpreted in terms of initial dose dependent rapid dye/heavy metal removal due to enhanced availability of binding ligands and larger surface area, while sluggish phase of dye/heavy metal removal might be the overlapping and shadowing effect of excess MPA particles on binding ligands and thereby, resulting into reduced

accessibility of the dye molecules/metal ions to the active site. The adsorption efficiency of MPA adsorbent in removal of cationic dyes was found to increase with gradual increase in pH (pH 4.0 – 10.0), whereas the acidic condition (pH 3.0) was favorable for the maximum adsorption of Cr(VI) by MPA. Adsorbent material (MPA) was found to be more effective in removal of cationic dyes and Cr(VI) in the pH range (pH 6.0 – 10.0) and (pH 3.0 – 4.0), respectively, due to combined action of physico-chemisorption and a reductive electron transfer reactions. Equilibrium adsorption isotherms (Langmuir and Freundlich) were applied on equilibrium adsorption data of cationic dyes and Cr(VI) and results showed monolayer physico-chemisorption of cationic dyes and Cr(VI), followed by both Langmuir and Freundlich adsorption isotherms. The maximum monolayer adsorption capacity (q_{max}) of MPA in removal of MG and MB dye was found to be 322.58 and 588.24 mg g^{-1}, respectively. In Cr(VI) removal by MPA, the q_{max} value was found to be 8.63 mg g^{-1}. The separation factor (R_L) values were between 0 and 1, indicating a favorable adsorption of cationic dyes and Cr(VI) onto MPA. Pseudo-first order, pseudo-second order kinetics and intra-particle diffusion model were analyzed at different concentration of cationic dyes and Cr(VI). The adsorption kinetic data fitted well with the pseudo-second order kinetics as the value of calculated q_e in this model was found to be very close to experimental value of q_e. Activation energy (*Ea*) calculated for the surface binding of MB (14.90 kJ.mol^{-1}) and MG dye (1.24 kJ mol^{-1}) indicated that the dye binding by MPA was energetically favorable physico-chemical sorption process. The values of Gibbs free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) for the sorption of cationic dyes and Cr(VI) onto MPA indicated that adsorption of dye/heavy metal by MPA was endothermic and spontaneous in nature. Further, use of desorbing agents like 0.1 N solution of HCl, H_2SO_4, CH_3COOH, NaOH and

H_2O exhibited better recovery of MG and MB dye from the MPA in the presence of HCl and H_2SO_4 than CH_3COOH, NaOH and H_2O. Present investigation revealed that removal of cationic dyes and Cr(VI) was due to synergistic action of physico-chemisorption coupled with reductive electron transfer mechanisms.