CHAPTER 3

MATERIALS AND METHODS

3. Materials and methods

3.1Adsorbent

3.1.1 Preparation of activated carbon from Mango kernel

The mango is a seasonal tropical fruit produced in several countries. Its global production during 2013 was around 43 million metric tonnes and India being its largest producer had a production of 18 million metric tonnes during the same year. The mango kernel is nearly 5% of the total fresh fruit weight. It is available almost throughout the country. At present the shell and its kernel is nothing but a waste of having no value. Since it is primarily lingo-cellulosic in nature, it would be interesting to use it as a feed-stock for making activated carbon for adsorption of water pollutants to save the woody biomass currently being used for producing activated carbon on large scale.

The mango seeds were collected from local fruit-vendors and were dried over a period of time. Thereafter, the dried mango stones were broken-up to retrieve the fleshy mango kernels from inside. The kernels were further dried and then crushed in the disintegrator. The crushed powder of kernel was sieved in 14-22 mesh (BSS) fractions to obtain the desired particle size of 710-1000µm and was selected for further operation. Then the mango kernels were washed twice to remove soluble and insoluble lighter materials and dried in an oven at 60˚C for overnight. Chemical activation of the precursor (powdered kernel) was done with 40% H_3PO_4 (Ar grade**).** The impregnation ratio of 3:1(weight of chemical: weight of powdered kernel, w/w) was used to ensure sufficient penetration and the mixture was kept undisturbed for 24 hrs at 35^{o}C. The kernel powder was then washed thoroughly with distilled water and dried in air oven at 75^{o}C for overnight.

The chemically activated dried kernel powder was carbonized at 600^{o}C in a laboratory muffle furnace (NSW India, NSW-101). Furnace temperature was raised at 20˚C/min to the final carbonization temperature 600 ^{o}C under inert atmosphere. The samples were maintained at the carbonization temperature for 1h before cooling to room temperature. The cooled carbonized mass was washed thoroughly with distilled water until the pH of filtrate water reached 7to ensure complete removal of residual acid and other organic and mineral matters, and then dried at 75˚C for overnight. The carbonized mango kernel activated carbon (MKAC) was kept in an airtight container for characterization and use in adsorption experiments.The activated carbon is abbreviated as “MKAC” throughout the manuscript**.**

3.1.2 Preparation of activated carbon from almond shell

Almond is a dry fruit which is produced in several countries including India. The shell of almond fruit is a very good agro-waste and excellent adsorbent. Since it is primarily lingo-cellulosic in nature and hard, it can be used as a feed-stock for making activated carbon for adsorption of water pollutants.

The almond shells were obtained from the local market. The shells were crushed in the disintegrator and sieved to obtain 14–72 mesh (BSS) fractions. Chemical activation of the powdered shells was performed with 40% H_3PO_4 (AR grade) using the procedure reported by Girgis *et al*. (2002).The impregnation ratio of 3:1 (weight of H_3PO_4: weight of powdered shells, w/w) was used for proper penetration and the mixture was kept for 24 h. The chemically mixed sample was dried in the oven at 70 °C for 10 h. The dried pre-treated almond shell powder was carbonized at two different temperature 600 °C and 700 °C for 2 hours in a laboratory muffle furnace (NSW India,NSW-101).The cooled carbonized samples were washed thoroughly with distilled water and its pH was adjusted to 7with 1N HCl and1N NaOH. The samples were then dried at 70 °C overnight. The carbonized almond shell activated carbon (ASAC1 for 600 °C and ASAC2 for 700 °C) thus obtained was kept in airtight bottles for characterization and adsorption experiments.

3.2 Adsorbate

3.2.1 Hexavalent chromium Cr (VI)

All the solutions were prepared using deionized water, and stock solution of 1000 mg/L Cr(VI) was prepared by dissolving potassium dichromate(analytical reagent [AR] grade). The test solutions of Cr (VI) were prepared by diluting the stock solutions to specific concentrations as per the requirements.

3.2.2 Methylene blue dye

The different dye solutions were made using Methylene Blue (Sigma -Aldrich, India) dye dissolved in double distilled water and this prepared solution was used as adsorbate in further experiments. The molecular mass of this MB dye is 373.9 g/mol and chemically represented as ($C_{16}H_{18}N_3SCl\cdot 3H_2O$). All other chemicals were commercially available with analytical grade.

3.3 Physicochemical characterization of activated carbon

The physicochemical characterizations of the prepared activated carbon samples were carried out in order to know their chemical composition, functional groups, morphology, and surface area. Various functional groups present on the surface of activated carbon were analyzed using a Fourier transform infrared spectroscopy (FTIR) analyzer (Scientific, Nicolet 5700).

The surface morphology was analyzed using scanning electron microscopy (SEM) (FEI™, Quanta 200F) to determine the surface texture and the porosity. The average pore size or diameter was also calculated using SEM results.

The elemental analysis of the almond shell powder and activated carbon were determined by using an elemental analyzer (Euro-EA). The surface area, pore volume and pore size of the almond shell powder and activated carbon were determined using the N_2 adsorption at -196 °C and N_2 desorption at ambient temperature with degassing at 300 °C using a Smart Sorbs 92/93 surface area analyzer (Smart Instruments Co. Pvt. Ltd.).

The pH value required to give zero net surface charge is pH_{pzc}. The surface is positively charged below this pH and negatively charged above this pH. A plot of the equilibrium pH versus initial pH yielded a curve from where the pH_{pzc} was identified as the point at which the change of pH is zero.

3.4 Adsorption study

For the determination of adsorption of adsorbate, the batch experiments are carried out. For execution of experiment, the stock solutions of hexavalent chromium, Cr (VI) (metal ion) and methylene blue (dye) are prepared by dissolving the respective adsorbates in distilled water. The required concentration of adsorbate solutions were prepared by dilution of the respective stock solution.

The adsorption experiments were conducted in 250 ml, Erlenmeyer flasks containing 100 ml solution of adsorbate to investigate the effects of contact time, solution pH, and initial concentration of adsorbate and dose of adsorbent. The pH of different adsorbate solution was maintained with the help of 0.1N HCL/NaOH solution. All adsorption experiments were carried out at a constant agitation speed of 150 rpm.

The residual concentration of Cr (VI) was determined by measuring the absorbance of the purple complex of Cr (VI) with 1, 5–diphenylcarbazide at 540 nm using a UV-spectrophotometer (Elico, SL 159). The difference in Cr (VI) concentration before and after the adsorption was used to calculate the percentage adsorption of Cr (VI). The residual concentration of methyene blue was also determined by UV-spectrophotometer at 665 nm.

The percentage removal (%) and adsorption capacity (q_e) was calculated using following equation

$$\%\ \text{Removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where C_0(mg/L) and C_e (mg/L) are the initial and equilibrium concentration of adsorbate respectively, V(L) is the volume of solution, W (g) is the mass of activated carbon, and q_e (mg/g) is the metal/dye uptake capacity of activated carbon.

3.5 Adsorption isotherms

Adsorption isotherms provide useful information, including the adsorption mechanism for the adsorption of adsorbate on the adsorbent surface, and are also important in the designing of adsorption systems. The two parameter isotherm models like Langmuir, Freundlich, Temkin and Dubinin–Radushkevich were used to analyze the equilibrium data obtained in the present study.

3.5.1Langmuir isotherm

The Langmuir isotherm model (Langmuir1918) is valid for the monolayer adsorption which assumes that all active sites of adsorption are homogeneous in nature and the adsorption at one site does not affect an adjacent active site of adsorption. The linear from of the Langmuir isotherm model is expressed by Eq. (3):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \tag{3}$$

Where, b is the adsorption equilibrium constant (L/mg) related to the energy of adsorption and q_m (mg/g) is the quantity of adsorbate required to make a single layer on a unit mass of adsorbent.

A further analysis of the Langmuir isotherm can be made on the basis of a dimensionless equilibrium parameter, R_L, also known as the separation factor and given by Eq.(4):

$$R_L = \frac{1}{1+bC_0} \tag{4}$$

Where, b is the adsorption equilibrium constant (L/mg) related to the energy of adsorption and q_m (mg/g) is the quantity of adsorbate required to make a single layer on a unit mass of adsorbent. The value of R_L lies between 0 and 1 for a favorable adsorption, while $R_L > 1$ represents an unfavourable adsorption, and $R_L = 1$ represents linear adsorption, while the adsorption operation is irreversible if $R_L = 0$.

3.5.2 Freundlich isotherm

The Freundlich model is an empirical equation which assumes that the active sites of adsorption are heterogeneous in nature and adsorption at one site affects the adsorption at the adjacent site. The linearized form of the Freundlich isotherm model (Freundlich, 1906) can be expressed as in Eq. (5):

$$ln\ q_e = ln\ k_f + \frac{1}{n} ln\ C_e \tag{5}$$

Where, K_f and n are the Freundlich isotherm constants. K_f (mg/g (L/mg)$^{1/n}$) indicates the adsorption capacity and n stands for the intensity of the adsorption.

3.5.3 Temkin isotherm

The Temkin isotherm model contains a factor that describes the interactions between adsorbent and adsorbate (Temkin and Pyzhev 1940; Dada et al. 2012). This model assumes that the heat of adsorption of all the molecules in the layer decreases linearly due the coverage of adsorbate molecules, and the adsorption of adsorbate is uniformly distributed. This model also assumes that the decrement in the heat of adsorption is linear rather than logarithmic, as used in the Freundlich isotherm model. The non-linear form of the Temkin model is given by Eq. (6):

$$q_e = \frac{RT}{b_t} \ln(A_T C_e) \tag{6}$$

The above equation can be simplified as given by Eq. (7):

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{7}$$

Where, B_T = (RT)/b_T, R is the universal gas constant (8.314 J mol/K) and T (K) is the absolute temperature. The constantb_T describes the heat of adsorption and A_T explains the equilibrium binding constant (L/min) corresponding to maximum binding energy. A graph of q_e versus ln$C_e$is used to calculate the Temkin isotherm constants, $A_T$and b_T.

3.5.4 Dubinin–Radushkevich isotherm

The D–R isotherm model is used to estimate the nature of the adsorption process, whether it is physical or chemical (Dada et al. 2012). The D–R isotherm is more general than the Langmuir isotherm because this model is not based on the assumption of a homogeneous surface or constant adsorption potential, but the apparent energy of adsorption is calculated. The D–R model is represented using the following non-linear Eq. (8):

$$q_e = q_m \exp\left(-K\varepsilon^2\right) \tag{8}$$

Where, K is a constant related to adsorption energy (mol^2/J^2). ε, the Polanyi potential is calculated from the equation, RT ln(1 + (1 / Ce)), where R (J/mol K) is the universal gas constant and T is the temperature. The mean free energy of adsorption (E) is calculated using Eq. (9):

$$E = \frac{1}{\sqrt{2K}} \tag{9}$$

The E value gives information about the adsorption type; if the value of E<8 kJ/mol the adsorption process is governed by physisorption, while for E> 16 kJ/mol chemisorption prevails.

3.6 Kinetic studies

In order to analyze the kinetics of the adsorption process, the equilibrium data were fitted to pseudo-first-order, pseudo-second-order and intra-particle diffusion models. To investigate the adsorption kinetic, experiments were performed at different initial concentrations of Cr (VI) and methylene blue at optimum conditions. The contact time was set for a particular time in each experiment to ensure each adsorption process could reach the equilibrium value.

3.6.1 Pseudo –first order

Lagergren proposed a model on pseudo-first-order kinetics (Kanjurang et al. 2017).The linearized-integral form of the pseudo-first order model is represented as Eq. (10):

$$ln(q_e - q_t)= ln\ q_e - k_1 t \tag{10}$$

where q_e and q_t are the sorption capacities at equilibrium and at time t (mg/g),respectively, and k_1 is the rate constant of pseudo-first-order sorption (min^{-1}). The values of k_1 and q_e can be determined from the slope and intercept of the graph of *ln* $(q_e - q_t)$ versus t.

3.6.2 Pseudo -second order

The pseudo-second-order sorption kinetics can be expressed as shown in Eq. (11):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{11}$$

where q_e and q_t are the sorption capacity at equilibrium and at time t (mg/g), respectively and $k_2$is the rate constant of the pseudo-second-order sorption (g/mg-min) which can be determined by plotting the graph oft/q_t versus t.

3.6.3 Intra-particle diffusion model

The intra-particle diffusion model was proposed by Weber and Morris (Weber and Morris, 1962) and describes information about mechanisms and rate controlling steps in the adsorption kinetics. This equation provides the information about rate-limiting step that appears in the adsorption process may be due to the diffusion of the adsorbate into the adsorbent layer. The model is represented using the following equation (12):

$$q_t = k_{id} t^{1/2} + I \tag{12}$$

Where k_{id} is the intra-particle diffusion rate constant (mg/g min$^{1/2}$), and the value of I(mg/g) represents the thickness of the boundary layer. The values of I and k_{id} are obtained from the intercept and slope of the curve, respectively.

3.7 Thermodynamic study

In order to find out the nature of the adsorption process, the mechanism, spontaneity and heat change in adsorption of Cr (VI) and methylen blue on activated carbon, it is important to determine relevant thermodynamic parameters. The enthalpy change, ΔH^o, entropy change, ΔS^o and Gibbs free energy change, ΔG^o, were determine using:

$$\Delta G^\circ = -RT \ln K_0 \tag{13}$$

$$\ln K_0 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{14}$$

Where T is the absolute temperature (K), R is the gas constant (8.314 J/mol K) and K_0 is the distribution coefficient calculated using the following equation:

$$K_0 = \frac{q_e}{c_e} \tag{15}$$

Thermodynamic properties were calculated by plotting the graph of $ln\ K_0$versus $1/T$. The intercept and slope of equation no.14 will provide the value of ΔS^o and ΔH^o respectively.