# OPTIMIZATION OF ECO-DERIVED ACTIVATED CARBONS / NANOCOMPOSITES IN SEQUESTERING ANIONIC DYES AND METAL ION - THERMODYNAMIC, KINETIC, STATISTICAL STUDIES

Thesis submitted to the Bharathiar University in partial fulfilment of the requirements for the award of the degree of

#### DOCTOR OF PHILOSOPHY IN CHEMISTRY

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### DEPARTMENT OF CHEMISTRY PSGR KRISHNAMMAL COLLEGE FOR WOMEN

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## Chapter IX

The thesis examines a thorough screening regarding the confiscation of aqueous dye/metal ion solutions viz., Direct Brown 2, Reactive Red 152, Cu(II) and their corresponding effluent samples. Two ecofriendly materials, one of plant origin, *Prosopis juliflora* bark (PJB) and one of animal origin, Goat Dung (GD) has been identified as potential sorbents. The collected aforesaid materials were modified with phosphoric acid/ sulphuric acid and activated in muffle furnace. The activated materials (PJBAC and GDAC) were sieved using 85 BSS scientific test molecular sieve. Physico-chemical characteristic studies were analyzed using specific methods. Elemental constitution and surface area of the prepared carbons were determined with CHNS analyzer, BET, BJH and Boem titration methods. Varied operating factors to establish the adsorption behaviour of six systems (DB2-PJBAC, RR152-PJBAC, Cu(II)-PJBAC, DB2-GDAC, RR152-GDAC, Cu(II)-GDAC) were studied by batch equilibration methods.

Scanning electron micrographs of both unloaded and sorbate loaded carbons were recorded to explore the surface morphological changes. Also, the sorption of Cu(II) was confirmed by EDAX analysis. FT-IR spectral analysis was performed to verify the participation of functional groups present on the surface of the derived carbons.

The operating conditions examined under batch mode include: varying initial concentration of aqueous dye/copper solutions, preset time intervals during the agitation process, pH of the medium, influence of cations, anions, co-ions and temperatures of the systems. Desorption and regeneration experiments were conducted to assess the economic viability of the systems.

Magnetic nanocomposites (PJBAC/GDAC–CFC) and photocatalytic composites (PJBAC/GDAC–TiO<sub>2</sub>) were synthesized using the carbon precursor and magnetization property/nanosize nature were confirmed from VSM and AFM data. Appropriate correlations between initial concentrations, dosages and solution pH as input and output variables were registered by the application of SPSS 20 software.

Adsorptive nature of the studied systems was established using Langmuir, Freundlich, Tempkin, DKR isotherm models. Pseudo first order, Pseudo second order

Chapter IX

kinetics, Elovich and intraparticle diffusion models were verified to recognize the rate of the adsorption process and understand the sorption dynamics.

Column experiments were performed using aqueous solutions to assess the quantification of the activated carbons. Elaborate study on desorption and regeneration of columns were carried out to assure the reusability of the exhausted materials.

Different textile industries located in Tirupur were surveyed to assess the extent of dye pollution. Two textile effluent samples from Texwell Pvt. Ltd located at Tirupur, Tamil Nadu, India were collected and subjected to batch and column studies, to describe the bulkiness of the system. Similar studies had been performed for sequestration of synthetically prepared Cu(II) solution. In order to judge the maximum efficiency of the chosen materials, an insightful comparison was made.

In regard to the batch/column procedure adopted, the following conclusions arrived at:

- Mesoporous nature of the prepared carbons was confirmed from the BET / BJH plots
- ➤ The SEM images of the sorbents before and after the sorbate removal implied a significant change supporting the occurrence of sorption. FT-IR spectra of dye/metal laden carbons refer to the participation of carboxylic acid, hydroxyl and phenolic groups
- Optimized conditions for the six systems, experimentally verified through batch process exhibiting maximum adsorption capacity at 85 BSS particle size and room temperature are:

DB2-PJBAC: 100 mg/L; 100 mg; 60 minutes; pH 6 - 49.2 mg/g

RR152-PJBAC: 100 mg/L; 150mg; 30 minutes; pH 6 - 23.6 mg/g

Cu(II)-PJBAC : 20 mg/L ; 60 mg ; 18 minutes; pH 6 - 17.1 mg/g

DB2-GDAC : 100 mg/L; 150 mg; 60 minutes; pH 6 – 30.6 mg/g

RR152-GDAC: 100 mg/L; 250 mg; 90 minutes; pH 6 – 17.7 mg/g

Cu(II)- GDAC: 20 mg/L; 80 mg; 15 minutes; pH 6 - 16.4 mg/g

- Adsorption of Cu(II) by the activated carbons were appreciably diminished by the presence of potassium ions in preference to sodium and magnesium ions. Similarly chloride ions was found to inhibit the sorptive efficiency of the carbons in comparison with sulphate ions for both the systems. Co-ionic studies revealed a marked influence in the removal of Cu(II) by Cr<sup>6+</sup> against Zn<sup>2+</sup>
- Desorption/ regeneration studies were observed to be more appreciable incase of PJBAC than GDAC
- ➤ The isothermal constants calculated from the derived linear plots of Langmuir and Freundlich isotherms indicated monolayer followed by multilayer adsorption under heterogeneous conditions. The equilibrium parameter 'R<sub>L</sub>' values and sorption nature 'n' values reflect on favourable adsorption process. Tempkin isothermal plot extended the nature of the adsorbate and adsorbent interactions. The mean free energy value obtained from DKR isotherm suggested physisorption for all the systems
- Kinetic studies revealed the fit in of the systems to pseudo second order model. Two phase sorption process, film diffusion and particle diffusion were described by intra particle diffusion model
- Thermodynamic parameters with negative  $\Delta G^{\circ}$  and  $\Delta H^{\circ}$ , positive  $\Delta S^{\circ}$  favoured the spontaneity, exothermic nature and increased disorderliness at the solid solution interface
- Column experiments as an extension of batch results favoured the quantification of the systems
- ➤ PJBAC and GDAC registered efficient removal of DB2, RR152 and Cu(II) from aqueous/synthetic environments and industrial effluent samples. Sorption efficiency of PJBAC was higher than GDAC, supported by the isothermal constants
- ➤ PJBAC CFC, GDAC CFC, PJBAC TiO₂ and GDAC TiO₂ recorded a maximum efficiency in the removal of DB2. Also, PJBAC-CFC recorded was found to better than GDAC-CFC
- Further DB2 was preferentially adsorbed by both the carbons than RR152

From the above observations it is summarized that the activated carbons and nanocomposites prepared from *Prosopis juliflora* Bark and Goat Dung are successful sorbents for the effective removal of DB2, RR152 and Cu(II) from aqueous solutions and industrial discharges. Further study is focused on the extension of sorption activity towards other classes of dye molecules and toxic metal ions, which pose a great threat to the environment.