Chapter XI

Conclusion

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The thesis is focussed on the thorough screening of enriched anions (phosphate, nitrate, sulphate) confiscation present in aqueous and wastewater samples. Four eco-friendly materials, three of plant-based debris: *Camellia sinensis* stem (CSS), *Elaeocarpus tectorius* seed (ETS), *Vicia faba* husk (VFH) and one from animal waste, *Gallus gallus domesticus* beaks (GGDB) had been identified in the process of ubiquitous removal of anions. These raw materials were collected from specific point sources, completely cleaned and modified using 0.1N hydrochloric acid, sulphuric acid and formaldehyde. The treated materials (TCSS, TETS, TVFH, TGGDB) were categorized into various mesh sizes and their particle sizes were confirmed microscopically.

Physico-chemical parameters of these prepared materials were analysed by standard specific methods. Surface acidic groups and surface area/ mean pore volume of the prepared sorbents' were determined using CHNS analyser, BET/BJH methods. The surface morphologies of unloaded and anion loaded sorbents', elemental constituents and participation of functional groups were recorded employing SEM, EDAX, FTIR techniques.

Operating factors viz., particle size, dosage, agitation time, initial anion concentration, pH, cations/co-ions and temperature of twelve systems: (PO_4^{3-}, NO_3^-, SO_4^{2-} - TCSS, TETS, TVFH, TGGDB), were experimentally verified by Batch equilibration method to assess the sorption characteristics and set up the equilibrium conditions. Isothermal models (Langmuir, Freundlich, Temkin and DKR), Kinetics (Pseudo-First-Order, Pseudo-Second-Order, Elovich and Intraparticle Diffusion), Thermodynamic nature were established to suggest the sorption mechanism, kinetic and equilibrium influence on the systems. The economic feasibility of the modified materials was explored by successive desorption/ regeneration studies. Batch variable data were correlated through statistical validation using SPSS 20 software.

Amongst the four tested materials, TETS and TCSS possessed excellent toxicants' trapping ability. In view of the promising sorption nature exhibited by TETS and TCSS, biofunctionalized beads were synthesized using calcium alginate, Goethite and magnetite

as precursors, resulting in the preparation of TETSCAB/TCSSCAB, G@TETS/G@TCSS and (M@TCSSB/M@TETSB).

Quantification of batch studies were manipulated through continuous column run for aqueous matrices and laundry effluent enriched with respective anions. Short term / long term column experiments at appropriate dimensions of TETS & M@TETSB were carried out as these prepared materials registered the best chelating property amongst all other synthesized sorbents. Column results were validated by corresponding kinetic models. Spent material was used as a bionutrient for phosphate solubilizing bacteria, which, in turn, enhanced the plant growth.

Results derived from batch/column operations are summarized as follows:

* Modified eco-friendly materials possessed mesoporous nature, confirmed by the BET / BJH analyses

* A significant variation on the surface of the sorbents in the pre and post experiments was evident from SEM images, favouring the sorption process, being confirmed by appearance of new peaks pertaining to specific anions in the EDAX spectra

* Involvement of certain functional groups viz., carboxyl, carbonyl, hydroxyl and other aromatic groups during sorption was supported by the recorded FTIR spectra of natant, modified materials

* Batch results suggested the optimum conditions of the varying parameters at which maximum sorbate removal had occurred at 0.18 mm particle size, initial anion concentration of 100 mg/L for PO_4^{3-}, NO_3^- and 250 mg/L for SO_4^{2-}, pH 5 and room temperature are:

  TCSS dosage: 200 mg - PO_4^{3-}, NO_3^- / 250 mg - SO_4^{2-} - 10 minutes agitation time

  TETS dosage: 100 mg -PO_4^{3-}, NO_3^- ; 150 mg - SO_4^{2-} - 5 minutes agitation time

  TVFH dosage: 200 mg - PO_4^{3-}, NO_3^- ; 250 mg -SO_4^{2-} - 10 minutes agitation time

  TGGDB dosage: 200 mg - PO_4^{3-}, NO_3^- ; 250 mg - SO_4^{2-} -15 minutes agitation time

* Notable results in the desorption/ regeneration studies were observed for TETS

* Amongst all the isotherm models employed, best linear fit was exhibited by Langmuir isotherm. Also, mean free energy values > 8kJ/mol as obvious from DKR isothermal plot imply that all the systems respond to physisorption

* Kinetic studies revealed the fit in of the systems to Pseudo second order model. Applicability of two-phase sorption process i.e., film diffusion and particle diffusion were described by intra particle diffusion model

* Thermodynamic parameters derived from Van't Hoff's plots of all the systems show negative ΔG^o and positive $\Delta H^o/\Delta S^o$ indicating spontaneity, endothermic nature and increased disorderliness at the solid solution interface of the sorption process

* Preferential order of anion sorption invariably by all the sorbents were in the order $PO_4^{3-} > SO_4^{2-} > NO_3^-$

* The order of sorption capacity of the studied materials based upon the factors discussed so far is TETS > TCSS > TVFH > TGGDB

* A comparison between the synthesized beads, using the best two sorbents viz., TETS, TCSS as precursors revealed M@TETSB to possess maximum anion sequestering property at a minimum dose level, with reference to other functionalized beads viz., TETSCAB, TCSSCAB, G@TETSB, G@TCSSB

* Morphological variations and appearance of new peaks in the anion laden M@TETSB against their unloaded counterpart were expressed as SEM and EDAX analyses. Further, appearance of new peak corresponding to iron-oxide, exhibition of crystalline nature pertaining to ferric ion, thermal stability / magnetic property of M@TETSB were established XRD, TGA - DTA and VSM techniques

* Quantification of sorbent's efficiency, met through column studies exposed TETS as a promising material, withstanding several desorption/ regeneration cycles, in the context of trapping of phosphate ions preferentially. Exhaustion of the column runs, exhibited immobilization of anions within TETS matrices, supported by the perfect fit of Yoon – Nelson model

* Scaling up of laboratory observations to field level was carried out through designing and installation of a prototype Fibre Reinforced Polymer column loaded with appropriate quantity of TETS at Perfect Laundry Unit, Ootacamund, Nilgiris, Tamil Nadu India. The outcome of the device performance was observed as, collection of 36 litres treated laundry wastewater containing a concentration of 1.2 mg/L PO_4^{3-} against the raw outlet concentration of 317 mg/L

* Phosphate loaded TETS material as consumed by phosphate solubilizing bacteria in agar medium was employed to germinate the seeds of mint leaves and radish. Conversion of the exhausted materials into a macronutrient ensured the non-disposal of the former as a solid secondary pollutant. The bionutrient quality of this culture to grow mint leaves and radish tubers was explicit against their control, as evident from better shoot heights of the nutrated plants. Non-bioaccumulation of the trivalent ion in the matured leaves, stems and roots of both the plants was experimented by wet digestion method. The derived samples were analysed in UV -Vis Spectrophotometer, wherein no traces of phosphate ion were recorded

* Future study is focussed on the implementation of fixed bed horizontal columns packed with magnetite beads at laundry units for effective chelation of phosphate ions from discharged wastewaters through a thorough agitation mode

* Chosen eco-based materials with apt modifications and the synthesized biofunctionalized beads registering excellent anion sorption efficacy, as aided by characterization studies, statistical data / isothermal / kinetics / thermodynamic analyses are the concluding remarks attained from the made observations, recorded results and detailed discussions presented in the thesis.