FUNCTIONALIZATION OF NOVEL BIO-ENCAPSULATED BEADS IN THE CHELATION OF NOXIOUS ANIONS AND FABRICATION OF FRP DEVICE AT LAUNDRY SITES – A GREENER APPROACH

Thesis submitted to Bharathiar University for the award of the degree of

DOCTOR OF PHILOSOPHY IN CHEMISTRY

Submitted By

K. VIVITHABHARATHI

Under the Guidance of

Dr. N. MUTHULAKSHMI ANDAL M.Sc., Ph.D.,

Assistant Professor

Department of Chemistry

DEPARTMENT OF CHEMISTRY

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Signature of the Supervisor
(Seal)
Dr(Mrs) N.Muthulakshmi An... M.Sc., M.Phil., Ph.D
Assistant Professor
Department of Chemistry
PSGR Krishnammal College for Women
Peelamedu
Coimbatore - 641 004

K. Vivi
Signature of the Researcher

D. Kalai
Head of the Department
(Seal)
Dr. D.NALINI M.Sc.,M.Phil.,B.Ed.,MCA.,Ph.D.
ASSISTANT PROFESSOR & HEAD
Department of Chemistry
PSGR Krishnammal College for Women
Peelamedu, Coimbatore - 641 004.

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(K. VIVITHABHARATHI)

Abstract

ABSTRACT

The unremitting industrial development has led to a subsequent increase in the amounts of wastewater generation. Fertilizer/ Laundry industries generate large volumes of wastewaters enriched with anions exceeding the standard limits, discharged into natural water bodies. Untreated disposal of these wastewaters pose serious threat to agricultural sector, aquatic life, human beings imposing adverse mutagenic/ carcinogenic effects. Removal of anions from these point sources poise as one of the major environmental concerns. Amidst, various methodologies tested for the reclamation of these anions, adsorption has been reported as a convenient method, due to many reasons such as flexible operation, specific toxicants' target and minimal generation of sludge. A number of zero cost and indigenous materials have been identified as promising sorbents to chelate the anions. The present study is focussed on the employment of *Camellia sinensis* stem (TCSS), *Elaeocarpus tectorius* seed (TETS), *Vicia faba* husk (TVFH) and *Gallus gallus domesticus* beaks (TGGDB), post relevant modifications as notable sequestrants for PO_4^{3-}, NO_3^- and SO_4^{2-}ions from aqueous and laundry wastewater samples. These modified materials are subjected to physio-chemical parametric determinations and characterized distinctly by BET/ BJH, SEM, EDAX and FT-IR techniques to assess their precise nature, during pros and cons of the experimental setup. The factors influencing the adsorption capacities of the derived materials are experimentally verified by Batch mode and quantified through column setup for aqueous anionic media at laboratory levels. Initial and residual concentrations of the studied anions are complexometrically analysed using UV - Vis Spectrophotometer. Experimental data pertaining to Batch equilibration studies are statistically verified using SPSS software. A judicious comparison is made to assess the best sorbing ability among the four selected materials and the order of preferential adsorption between the three chosen anions. Desorption and regeneration experiments are performed for anion laden sorbents to enumerate their reusable property. Varied isothermal / kinetic models, dynamic behaviour of the verified systems is validated to understand the adsorption equilibrium and kinetic / thermodynamic behaviour. Calcium alginate, goethite and magnetite functionalized bio-beads are synthesized and characterized using XRD, TG-DTA and VSM methods. Sorption efficacies of these synthesized beads are recorded by

pilot studies and extended to column verification, followed by kinetic model validation. Exhausted column material is tested for its nutrient value in plant vegetation using phosphate solubilizing bacteria, thereby minimizing its load as a secondary pollutant. Based on the laboratory recordings, a prototype device is designed and installed at a laundry unit to promote the applicability of the novel material as an excellent sorbent at the field level.

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LIST OF ABBREVIATIONS AND NOTATIONS

CSS	*Camellia sinensis* Stem
ETS	*Eleocarpus tectorius* Seed
VFH	*Vicia faba* Husk
GGDB	*Gallus gallus domesticus* Beaks
CPCB	Central Pollution Control Board
TCSS	Treated *Camellia sinensis* Stem
TETS	Treated *Eleocarpus tectorius* Seed
TVFH	Treated *Vicia faba* Husk
TGGDB	Treated *Gallus gallus domesticus* Beaks
SEM	Scanning Electron Microscope
BET	Bruner Emmett Teller
BJH	Barrett Joyner Hammett
FT-IR	Fourier Transform Infrared Spectrophotometer
EDAX	Energy Dispersive X-ray Spectrometer
UV - Vis	Ultra Violet Visible Spectrophotometer
VSM	Vibrating Sample Magnetometer
M_s	Saturation Magnetization
XRD	X-Ray Diffraction
TGA	Thermo Gravimetric Analysis
DTA	Differential Thermal Analysis
ZPA	Zeta- Potential Analyzer
PSA	Particle Size Analyzer
Conc.	Concentration

pH_{zpc}	pH at which the surface charge of the adsorbent is zero
q_e	Amount of anions adsorbed per gram of the adsorbent (mg/g)
C_i	Initial anion concentration (mg/L)
C_e	Equilibrium anion concentration in solution (mg/L)
R^2	Correlation Coefficient
q_e	Amount of anions adsorbed per gram of adsorbent at equilibrium (mg/g)
q_t	Amount of anions adsorbed per gram of adsorbent at time ‘t’ (mg/g)
q_m	Maximum monolayer adsorption capacity (mg/g)
B	Langmuir Adsorption Constant
K_F	Freundlich Adsorption Capacity (mg/ g)
N	Freundlich Isotherm Constant
A_T	Temkin Equilibrium Binding Constant
b_T	Temkin Heat of Adsorption
R	Gas Constant (8.314 J/mol K)
β_{DR}	Mean free energy of sorption per mole of adsorbate (mol^2/J^2)
ϵ	Polanyi Potential
ε	Mean Free Energy (kJ/mol)
k_1	Pseudo First Order Adsorption Rate Constant (min^{-1})
k_2	Pseudo Second Order Adsorption Rate Constant (g/mg min)
SSE	Sum of Error Squares
α	Elovich Initial Adsorption Rate (mg/g min)
β	Elovich Adsorption Constant (g/mg)
K_i	Intraparticle Rate Constant (g/mg $min^{1/2}$)
$\Delta G°$	Gibb’s free energy change of adsorption (kJ/mol)

$\Delta H°$	Enthalpy change of adsorption (kJ/mol)
$\Delta S°$	Entropy change of adsorption (J/mol K)
K_T	Thomas Constant (L/mg min)
q_T	Adsorption capacity (mg/g)
Q	Volumetric flow rate (mL/min)
M	Mass of the adsorbent (g)
C_0	Initial Concentration (mg/L)
C	Effluent Concentration (mg/L)
K_{AB}	Kinetic Constant (L / mg min)
F	Flow rate (mL / min)
Z	Bed depth (m)
N_0	Saturation constant (mg/L)
t	time
C_0	Influent concentration (mg/L)
C_i	Effluent concentration (mg/L)
K_{YN}	Velocity constant (L / min)
τ	Time required for 50 % of adsorbate breakthrough
t	Sampling time

List of Instruments / Equipments used for Various Studies

LIST OF INSTRUMENTS / EQUIPMENTS USED FOR VARIOUS STUDIES

1. UV – Visible Spectrophotometer
2. BET Surface Analyzer
3. CHNS Analyzer
4. Scanning Electron Microscope
5. Energy Dispersive X- ray Spectrometer
6. Fourier Transform Infrared Spectrophotometer
7. Ocular Micrometer
8. X-ray Diffractometer
9. Vibrating Sample Magnetometer
10. Thermo Gravimetric – Differential Thermal Analyzer
11. Thermostat Controlled Mechanical Shaker
12. Digital pH Meter