Annexure-XI

UNIVERSITY GRANTS COMMISSION

BAHADUR SHAH ZAFAR MARG

NEW DELHI – 110 002

Final Report Assessment / Evaluation Certificate

(Two Members Expert Committee Not Belonging to the Institute of Principal Investigator)

(to be submitted with the final report)

It is certified that the final report of Major Research Project entitled "**Removal of fluoride using new hybrid sorbents of polymers-mixed metal oxides: development of fluoride removal kit for rural use**" by **Dr./Prof. RATAN KUMAR DEY** Dept. of Chemistry, Central University of Jharkhand, Ranchi, has been assessed by the committee consisting the following members for final submission of the report to the UGC, New Delhi under the scheme of Major Research Project.

Comments/Suggestions of the Expert Committee:-

The project focused on development of new adsorbents for the removal of fluoride from dilute aqueous solution. The prepared adsorbent materials were characterized and applied for defluoridation of drinking water. Based on literature studies and other available references, attempt was made to prepare and evaluate some newer kind of adsorbents using simple laboratory procedure. In this context, in this work, preparation of hybrid materials (from combination of new polymeric host and fluoride specific element such as zirconium), porous materials from modification of waste bio-resources and from gel materials prepared using newly developed technique/procedure. All such materials were intended to explore the material properties and hence to utilize the defluoridation capacity especially from drinking water. Thus, the work presented is focused on following aspects:

(i). Preparation of Shellac – Zirconium hybrid material.

27/7/2022

Dr. S. Mishra 27/7/2022

(ii). Development of Pea (*Pisum sativum L.*) peel waste carbon – Zirconium hybrid material.

(iii). Development of $Al_2O_3 – ZrO_2$ xerogel material.

All materials were characterized using advanced instrumentation techniques. The kinetics and thermodynamics aspects of the studies were carried out with optimization of parameters such as solution pH, adsorbent doses, solution concentration and temperature. Most importantly, the materials shows the good adsorption characteristics within pH 6.0 – 7.0 at ambient temperature conditions.

The specific conclusions drawn from the work can be summarized as follows:

The new hybrid material (ShZ) prepared from combination of shellac (Sh), a natural biopolymer, and zirconium (Z) for the defluoridation of drinking water uses environment friendly sol-gel technique. Material characterization using FTIR provides the spectral information regarding shifting of $\nu(O-H)_{str}$ towards lower wave number indicating successful attachment of fluoride to the prepared ShZ material surface probably through a weak van'der Waal's bonding. The incorporation of zirconium to the polymeric shellac material was further evidenced by study of Scanning electron micrographic spectra associated with energy dispersive spectrum (EDS) measurement technique. The X-Ray Diffractogram (XRD) indicates the amorphous characteristics of material. The defluoridation characteristic of hybrid material was evaluated by variation of number of solution parameters. It was observed that the fluoride sorption characteristics was very fast within first 5 minutes time interval where almost 60% of fluoride removal could be possible from a 10 mg L^{-1} fluoride solution at natural pH of the medium (pH = 7.0). The adsorption process attained equilibrium in 40 minute with almost 97% removal of fluoride using 0.2 g L^1 of material. The process follows pseudo-second order kinetic as well as intra-particle diffusion model with almost ≥ 0.99 accuracy. The thermodynamics of fluoride adsorption was found to be spontaneous and exothermic in nature. The sorption characteristics of the material follows ligand exchange mechanism. The new material ShZ shows good regeneration efficiency up to 6^{th} cycles of continuous operation with very little effect of co-ions which can be helpful for its' commercial applications.

27/7/2020

Dr. S. Mishra 27/7/2020

Pea peel waste carbon – loaded with zirconium is used as an engineered biochar material for adsorption of fluoride from aqueous solution. The adsorbent was characterized using the Fourier Transform Infrared Spectrophotometer (FTIR), Scanning Electron Microscopy and Energy Dispersive X-Ray spectroscopy. The material degradation kinetics was studied with programmed temperature enhancement in a Thermo-Gravimetric Analysis (TGA) system using mathematical models. The material-anion equilibrium in a solution is reached in 55 minutes by use of optimized amount (0.3g) of material in an ambient temperature (25°C) and natural pH (7.0) conditions and maximum 97% fluoride removal was observed. Adsorption kinetics follows both pseudo-second order as well as intra-particle diffusion model with close agreement of $q_{e,exp}$ and $q_{e,cal}$ values and highest correlation coefficient (R^2 = 0.9922). Adsorption of anion favors Freundlich isotherm, result of which is refined using linear least square method and optimization of algorithms. Both endothermic nature of adsorption (positive ΔH) and its spontaneity (negative ΔG), calculated from thermodynamics equations, correlated with the activation energy and sticking probability to determine the nature of sorption of fluoride onto the material surface. A negligible effect of co-ions (chloride, nitrate and sulfate) was observed using appropriate amount of solute. The adsorbent is capable of leaching of adsorbed fluoride using 0.001N NaOH and reuse (up to 10th cycle of continuous operation) demonstrating its potential commercial viability for fabrication of defluoridation kit.

Continuing with the investigations, attempt was made to use a composite xerogel material (Al_2O_3/ZrO_2) for defluoridation of drinking water. Use of composite xerogel in fluoride removal is a completely new and innovative. Here, the material was prepared by environment friendly sol-gel technique using respective metal salts as precursors, thus avoiding use of toxic and expensive metal alkoxides as precursor materials. FTIR spectra of the material indicated presence of bridged structure of Zr – O – Al in the material. Decrease in intensity of hydroxyl group vibration indicates substitution of surface hydroxyl groups by fluoride through formation of metal – fluoride bonding. The XRD of material showed amorphous characteristics of Al_2O_3/ZrO_2. The morphological feature of the material indicate presence of micro-pore in the structure. The total specific surface area ($m^2 g^{-1}$) and average pore radius (nm) were calculated to be 3.68 and 1736.6,

27.7.2020
Dr. S. Mukherjee

respectively. The kinetics of thermal degradation pattern of the materials indicates heterogeneous process and the molecular interaction/bonding between aluminum-zirconium contributed in enhancing the stability of the material. Material-anions equilibrium was attended within 20 minutes time interval with 98% of fluoride adsorption efficiency. Fluoride adsorption characteristics was found to be pH dependent influenced by pore diffusion. The presence of multiple active centers, *i.e.*, Al and Zr in Al_2O_3/ZrO_2 favors fluoride sorption characteristics in comparison to ZrO_2 xerogel. Fluoride adsorption follows pseudo-second order kinetic as well as intra-particle diffusion model with almost ≥ 0.99 accuracy. The thermodynamics of fluoride adsorption was found to be spontaneous and exothermic in nature. The adsorbent shows good regeneration efficiency up to 5^{th} cycles of continuous operation with very little effect of co-anions which can be helpful for its potential commercial applications.

In general, the progress of the work within stipulated time frame resulted in development of new adsorbent materials which could able to remove more than 90% of fluoride from water sample. A comparative aspects with respect to other published reports/commercial materials were made. The progress of the work has been according to the original plan of work and towards achieving the objective. In addition, the researcher could also able to do some extended experimental works that can be helpful for future aspects of new material development and application for defluoridation which is also available as published report. The experimental results were analyzed and published in following International Journals of repute:

(i) Pea (*Pisum Sativum L.*) peel waste carbon – loaded with zirconium: study of kinetics, thermodynamics, and mechanism of fluoride adsorption – manuscript submitted to **Separation Science and Technology** (Taylor & Francis). 14 (2019) 2194 – 2211. **Impact Factor: 1.36**

(ii) Development of aluminum and zirconium based xerogel for defluoridation of drinking water: study of material properties, solution kinetics and thermodynamics, **Journal of Environmental Chemical Engineering,** 6 (2018) 6231 – 6242. **Impact Factor: 4.30.**

27/7/2020

27.7.2020
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(iii) Development of new zirconium loaded shellac for defluoridation of drinking water: Investigations of kinetics, thermodynamics and mechanistic aspects, **Journal of Environmental Chemical Engineering**, 4 (2016) 4263 – 4274. **Impact Factor: 4.30.**

(iv) Kinetics and thermodynamics of defluoridation of drinking water using high performance hybrid Zr(IV)-hexamethylenediamine: a comparative aspect with ion-exchanger amorphous zirconium(IV) phosphate, **Surfaces and Interfaces** (Elsevier), 13 (2018) 22 – 32. **Impact Factor: 3.72.**

Few of the studies that needed to be done can be enlisted as follows:

(i) Application of materials in column operation with variation of parameters.
(ii) Evaluation of biological characteristics of treated water.
(iii) Evaluation of process cost and material cost.
(iv) Study of safe disposal of exhausted adsorbents.

It is suggested that all these above studies can be taken up by researcher in collaboration with institute/universities so that necessary expertise can be incorporated in the work for future commercial development and applications.

Hence, the above mentioned task can be accomplished by seeking extension of the project (or) applying some new project with requisite technical input towards commercialization of the products.

27/7/2020

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Hence, in our considered opinion, the work carried out by the Principal Investigator of the project is quite exhaustive within limited time frame. The scientific output of the project (available as publications/summary of the project) can also be used for undertaking new initiatives.

Name & Signatures of Experts with Date:-

Name of Expert	University/College name	Signature with Date
1. Dr./Prof.B.K.Agarwal **Chief Scientist-cum-Univ.Professor**	**Dept. of Soil Science** **Birsa Agricultural University, Ranchi**	27/07/2020

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2. Dr./Prof. Sumit Mishra **Dept. of Chemistry**
Birla Institute of Technology, Ranchi

It is certified that the final report has been uploaded on UGC-MRP portal on: Dt. 02/~~JULY~~/SEPT/2020

It is also certified that **final report**, **Executive summary of the report**, Research documents, **monograph academic papers** provided under Major Research Project **MRP 42-264/2013 (SR)** have been posted on the website of the University/College.

02/9/2020

(Registrar/Principal)
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REGISTRAR
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