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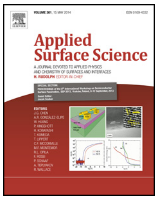

Surface restructuring of lignite by bio-char of *Cuminum cyminum* – Exploring the prospects in defluoridation followed by fuel applications

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ABSTRACT

Recently, there has been an interest in the areas of developing new carbon materials for fluoride removal applications. The development of new carbon materials is of recent choice which involves the synthesis of hybrid carbon from various sources. In this context, the present contribution is made to focus on the study the restructured surface of lignite using a bio-material called *Cuminum cyminum*. The restructured lignite (RSL) was synthesized with an improved carbon content of 13% and its BET surface area was found to be 3.12 times greater than lignite (L). The amorphous nature of lignite and RSL was quite explicable from XRD studies. SEM studies exhibited a fibrous and finer surface of lignite which was well restructured into a semi-melt (5 μm) surface for RSL. Defluoridation potential of Restructured Lignite (15.8 mg g^{-1}) was greater than the lignite (13.8 mg g^{-1}) at pH 7.93 ± 0.03. Kinetic and isotherm parameters derived from various models helped in comprehending the nature and dynamics of fluoride sorption. Both the normal and the restructured lignite were found to be consistent with its fluoride uptake of 57% and 60% respectively even after fifth cycle of regeneration. High heating values of 22.01 MJ kg^{-1} and 26.90 MJ kg^{-1} respectively for lignite and RSL deemed their additional application as fuel materials.

Introduction

Water, an essential natural resource, gets degraded in its quality over the past few decades due to population growth, urbanization, industrialization and improper utilization water resources leading to reduction in its per capita availability in various developing countries [1–3]. About 80% of the diseases in the world are caused due to deteriorated quality of water. Fluoride concentration in groundwater depends on the variables *viz.*, geochemistry, physico-chemical characteristics of the aquifer, porosity and acidity of the soil and rock and the associated temperature dynamics of the aquifer. The fluoride concentration in groundwater ranges between 1 mg L^{-1} and 35 mg L^{-1} across different countries (WHO, 2008) [4]. In the world, fluoride contamination in drinking water causes 65% of endemic fluorosis which affects teeth, bones and soft tissues [5,6]. Especially to young children, fluoride within permissible limit of 1.0–1.5 mg L^{-1} is essential for dental enamel calcification. In several Countries, addition of fluoride (1.0 mg L^{-1}) to public drinking water supplies is in extent for the mitigation of dental caries and strengthening of bones is still practiced [7,8]. High fluoride in drinking water across 25 developed and developing Countries has been reported which include Pakistan, China, Sri Lanka, West Indies, Spain, Holland, Poland, Italy, Mexico, Thailand, Eritrea (North East Africa), West Africa, Southern Africa, North America, South America and India [9–14]. According to Bureau of Indian Standards (BIS, 2009) [15], the permissible limit of fluoride is 1 mg L^{-1} in drinking water. In India, at least 230 districts in 19 States are affected by fluorosis. The States are Andhra Pradesh, Gujarat, Rajasthan, Karnataka, Orissa, Punjab, Maharashtra, Madhya Pradesh, Haryana, Bihar, Tamil Nadu, Uttar Pradesh, West Bengal, Kerala, Assam, Delhi, Jammu and Kashmir, Jharkhand and Chhattisgarh [16]. The upper limit of fluoride recommended by World Health Organization is 1.5 mg L^{-1}. The target organs for fluoride are bones and teeth which tend to accumulate with respect to age [7,17,18]. Endemic dental hypoplasia (tooth discoloration), enamel hypoplasia and linear enamel hypoplasia (LEH) are some of the diseases which are categorized under dental fluorosis. Skeletal fluorosis, a crippling disorder is permanent and irreversible in nature and its effects are detrimental in nature to the health of an individual and community by way of affecting growth, development, economy and human resources.

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Defluoridation studies using various techniques such as adsorption [19], nano filtration [20,21], electro-coagulation [22], membrane separation [23], donnan dialysis [24], membrane coagulation reactor (MCR) [25], ion-exchange process [26] and hybrid precipitation–microfiltration [27]. Though fluoride removal is facilitated through advancement in technologies, the most preferred, economical and widely used method is adsorption. Surface properties such as large surface area and continuous porosity possessed by porous carbons govern their sorption potential. In the recent past, papers on calcium [28,29], aluminum oxide [30], magnesia [31] and cerium-supported carbons [32] (prepared from various biomass) are of great interest by researchers. Manganese-oxide coated carbon [33] and graphene oxide [34] sorbents were also attempted which lead to improved defluoridation potential of carbon adsorbents. Also the natural presence and appreciable participation of calcium (as carbonate) in *Tamarindus indica* fruit shell carbon was explored through fluoride removal studies [35]. Srimurali et al. [36] reported the fluoride uptake capacity of raw lignite (3.95 mg g^{-1}) and compared with other low cost sorbents. The defluoridation efficiency of a low grade Assam coal was reported to be 85% by Borah and Dey [37]. Sivasamy et al. [38] and Miloslav [39] attempted defluoridation using coal-based sorbents and natural lignite at Vienna basin respectively. The application of lignite is multifarious with respect to its physical properties such as proximate and ultimate analyses, surface area and porosity. Liu et al. [40] investigated the combustion efficiency of hydro char–lignite due to synergetic interaction between hydro char and lignite. The modification in physical and chemical properties due to the addition of biomass with lignite was addressed by Liu [41] along with enhanced combustion properties of the hydro char–lignite blend. By keeping the dual profile of carbon materials in mind, the study was firstly concentrated on the restructuring of lignite and its fluoride removal capacity. Secondly, the spent restructured lignite was recycled for five times and then analyzed for its combustion properties. Hence the present contribution was not only limited to the application on fluoride removal but also extended as a material which finds application as a solid fuel possessing appreciable combustion properties.

Experimental

Preconditioning and restructuring of lignite

The precursor, waste lignite was procured from a power generating industry located in the Neyveli area, Tamil Nadu, India. Initially the precursor of 200 g was washed with double distilled water till the washings of lignite became colorless. Then the wet mass was dried at 110 ± 5 °C for about 24 h. The dry mass of waste lignite was then treated with concentrated H_2SO_4 and maintained under digestion for 5 h. The digested mass was washed with double distilled water till neutral pH was attained for washings. The resulting wet mass of lignite was dried at a temperature of 110 ± 5 °C for 5 h and used for defluoridation experiments.

Cumin (*Cuminum cyminum*) seeds were washed several times with de-ionized water to remove the dust particles which present along with the biomass and then air dried. The air dried seeds were pulverized and the resulting ground mass of 100 g was prepared in the form of slurry in 250 mL double distilled water. To the slurry, 100 g of L was added at intervals and stirred for 10 h to ensure uniform mixing. The resulting wet mixture was dried at 110 ± 5 °C for 5 h and then the dry mixture was under thermal treatment in the muffle furnace at 400 °C for 3 h. The yielded black mass was washed using double distilled water and once again dried at 110 ± 5 °C. The restructured lignite (RSL) by the above hydrothermal treatment [42] was used for defluoridation experiments.

Characterization of the adsorbents

Proximate analysis for the adsorbents Lignite (L), *C. cyminum* (CC) and Restructured Lignite (RSL) was carried out according to the Standard Practice for the Proximate Analysis of Coal and Coke (GB/T212 – 1991) using a MAC – 500 Proximate Analyzer (LECO make, USA). The ultimate analysis for carbon, hydrogen, nitrogen and sulfur contents carried out on a C4N – 600 Elemental Analyzer LECO make (212 μm – 1 g – ASTM 5142 – 90). The adsorbent materials were observed and analyzed by Scanning Electron Microscope (SEM) with a JEOL JSM model 5610 microscope to study its surface morphology. Powder X-ray diffraction (XRD) patterns were collected with a INEL XRG 3500 diffractometer using Cu Kα (λ = 1.540560 Å) at 30 kV and 30 mA with an angle range 2θ between 5° and 120° and step length of 0.02° (2θ). The specific surface of L, CC and RSL was determined by nitrogen adsorption/desorption at 77.5 K on a Micromeritics ASAP 2020, V4.00 H instrument.

Adsorption experiments

The batch adsorption systems were conducted using analytical grade (AR) chemicals. Stock fluoride solution of 100 mg L^{-1} was prepared initially and using which different standard solutions was prepared according to experimental requirements. To establish the accuracy, reliability and reproducibility of the collected data, all the batch tests were replicated thrice and the experimental blanks were run in parallel and the average values are reported. pH of various fluoride solutions was adjusted using pH meter (LI 120, Elico Model) with 0.01 N of HCl or NaOH. An equilibrium time of 220 min was optimized for shaking and the residual fluoride concentration was determined thanks to a fluoride ion selective electrode (Orion, number BN 9609, USA) connected to an ion meter (Orion, model 290A, USA). After the optimization of pH, sieve size and dose, every kinetic study was conducted with 100 mL of sodium fluoride solution with an adsorbent dose of 20 g at room temperature. The co-ion interference study was conducted with 3 mg L^{-1} of fluoride concentration mixed with 200 mg L^{-1} each of the sodium salts of bicarbonate, nitrate, chloride, sulfate and phosphate to form a heterogeneous solution system of F^-/HCO_3^-, F^-/NO_3^-, F^-/Cl^-, F^-/SO_4^{2-} and F^-/PO_4^{3-}. Regeneration study was carried out with an initial fluoride concentration of 3 mg L^{-1} using 20 g per 100 mL of the spent L and RSL for 120 min. Field trials were conducted for selected groundwater samples under the same conditions adopted for the synthetic fluoride solution. Thermodynamic parameters of adsorption *viz.*, standard free energy change (ΔG°), standard enthalpy change (ΔH°), standard entropy change (ΔS°), activation energy (E_a) and sticking probability (S^*) were calculated at 303 K, 313 K and 333 K.

Results and discussion

Characterization of lignite (L) and restructured lignite (RSL)

The results after proximate and ultimate analyses, flammability index, and high heating values are shown in Table 1. The carbon content for L and RSL of 51.96% and 65.16% respectively, revealed that the restructuring improves the carbon content up to 13% and these can be good precursors to prepare activated carbon [43].

The HHV of L and RSL are 22.01 MJ kg^{-1} and 26.90 MJ kg^{-1} respectively. As the HHV values exceed 20 MJ kg^{-1}, the above materials are ensured for auto-thermal combustion and can be suggested as promising alternatives for solid fuel applications. In general, biomass feed stocks have low calorific values and high oxygen contents when compared to coal. When the biomass is co-combusted together with coal, there seems an appreciable result in