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Fluoride Removal from Aqueous Solutions via Adsorption Using Raw, Calcined, and Chemically Treated Laterite Mineral

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ABSTRACT

Accessing safe drinking water in India faces a mounting challenge due to deteriorating water quality from industrial pollution and excessive groundwater extraction, leading to increased chemical impurities like fluoride affecting 66 million people across 20 states. Fluoride contamination, arising from natural sources like volcanic activity and mineral weathering, is compounded by industrial discharge from semiconductor, metal, glass, and fertilizer industries. Prolonged exposure to fluoride-laden water poses health risks, causing dental, skeletal, and non-skeletal fluorosis. To address these risks, the World Health Organization (WHO) set the acceptable fluoride limit in drinking water at 1.5 mg/l. Despite various available technologies like coagulation and membrane processes, adsorption remains the most cost-effective method, especially for domestic use. Materials such as alumina, zeolite, clay, coal, and ceramics have been studied as fluoride adsorbents. In present study, laterite, bauxite, hematite, and calcite minerals rich in iron, aluminum, silica, and calcium were examined for fluoride ion adsorption at 7 pH and room temperature. Laterite displayed superior adsorption capacity compared to other minerals. Parameters like stirring speed, adsorbent size, and thermal treatment were investigated for their impact on laterite's adsorption capacity. Raw laterite was successfully modified by loading it with copper oxide using a copper sulphate solution, significantly elevating its adsorption capacity from 0.26 to 1.905 mg/g, an eight-fold increase. Freundlich isotherm analysis confirmed multilayer adsorption facilitated by electrostatic forces. Isotherm study validates that surface-modified laterite is a robust adsorbent for fluoride removal at neutral pH and room temperature, presenting a promising solution for water treatment needs.

Key words: Fluoride, Adsorption, Laterite, Kinetics, Isotherms

INTRODUCTION

Accessibility of potable water is rising problem in India. Reason being deteriorating water quality from sources and industrial pollution. Individuals are using various water treatment units but are unable to produce potable water. Growing population, urbanization and increasing water demand for industry, agriculture, hydroelectricity and drinking have brutally impacted the water quality (Anonymous 2014, Khurana and Sen 2007). Increased use of groundwater also started impacting its quality. Its Over-extraction has resulted in increase in many chemical impurities like fluoride, arsenic, aluminium, nitrates, iron, copper, blockishness etc. Fluoride in drinking water has affected around 66 million people of 20 states of India (Anonymous 2012, Shimelis et al. 2006).

Fluoride (F^-) is considered as one of the most common impurities of water. Volcanic eruption and weathering of fluoride containing rocks and minerals are natural source of F^- in water. Other sources of F^- contamination are release of effluents in water from industries like semiconductor industry, metal, glass, and fertilizer industry. Dental, skeletal, and non-skeletal fluorosis are detrimental health hazard of prolonged exposure of F^- contaminated drinking water. Due to these ill effects, World Health Organization (WHO) has given acceptable limit of F^- in drinking water is 1.5 mg/l (Meenakshee and Maheshwari 2006, Mohapatra et al. 2009).

Various technologies are currently available to remove fluoride from water, such as coagulation and precipitation, membrane processes, electrochemical treatments, ion-exchange, but the adsorption process is largely accepted as the cheapest and most effective method for removal F^- from water especially for domestic water treatment. Various materials, tested as adsorbents, were alumina, bauxite, zeolite, Kaolin, montmorillonite, Bentonite clay, laterite, coal, ceramic, pumice etc (Saxena and Sewak 2015, Kabir et al. 2019).

From literature, it is noticed that aluminium, iron, calcium and silica-based adsorbents are used for fluoride removal. Based on these, in current work, bauxite, calcite, hematite and laterite mineral adsorbents are selected for F^- removal study. Laterite was found to have more adsorption capacity over other selected mineral. Adsorption capacity of laterite was compared with commercially available F^- removal activated alumina and aeon adsorbent. Different adsorption parameters like effect of stirring speed, F^- concentration, adsorbent size, thermal treatment, and chemical treatment on surface modification to increase adsorption capacity of laterite were studied.

Laterite ore is rich in aluminium and iron. All laterites are in rusty red colour due to high concentration of iron oxides. Laterite is cost effective and hence can be considered as an alternative adsorbent for defluoridation (Sarkar et al. 2006). Sujana et al. (2019) conducted batch experiments on geomaterial laterite with low and high iron containing nickel and overburden of chromite mines from Orissa Mining Corporation to evaluate defluoridation capacity. Raw laterite sorption capacity passed to maxima at acidic pH. Drastic decrease in AC was reported with increase in pH with acid treated laterite by Maiti et al. (2011). Acid treated laterite mineral of Kenya was reported as chemically stable adsorbent with F^- removal efficiency as 60 to 80% at wide range of aqueous pH (2-8) conditions (Wambu et al. 2012). Variation in laterite chemical and mineralogical composition affect its F- adsorption mechanism (Juliet et al. 2015).

MATERIALS AND METHODS

Bauxite, calcite, hematite and activated alumina are purchased from Alminrock, Bangalore. Laterite adsorbent was purchased from local brick shop of Mangaon, Raigad, Maharashtra. Sample of aeon adsorbent was received from Aeon Procare Pvt Ltd, Gujrat. Mineral samples were first crushed in ball mill and then sieved in sieve shaker. These samples were then washed with distilled water to remove earthy materials and then dried in hot air oven at 105°C. This sample is referred as pre-treated mineral sample. Initial and final F- concentration was analysed using Thermo Scientific Orion Star Bench Top Fluoride Meter.

Batch adsorption experiments

Adsorption of F^- from its aqueous solution on adsorbent were performed using standard solution of sodium fluoride NaF without presence of any competing anions. Adsorption runs were carried out in 250 ml flask by dispersing certain amount of adsorbent samples in 100 ml of 2.5–25 mg/l of fluoride solutions. All the adsorption experiments were carried out at ambient temperature (27± 2°C) and pH ~ 7. After continuous shaking for a determined time interval, the solid was separated by filtration and the remaining fluoride was analysed using Fluoride Meter. Effect of adsorbate dosing, stirring speed, adsorbent size, calcination temperature and chemical dosing on surface modification were studied to improve adsorption process.

Chemical treatment of laterite by $CuSO_4$

Ten grams of sieved laterite was added in 100 ml copper sulphate ($CuSO_4$) solution of varied concentrations from 0.005–0.05 M to optimize chemical dosing. NaOH (0.1 N) was added to maintain solution of pH at 5. Then solution was agitated continuously in shaking thermostat at room temperature for 8 hrs. After agitation, solution was filtered and adsorbent was thoroughly washed with distilled water to eliminate extra copper sulphate. The washed adsorbent was air dried for 4 hrs and subsequently was calcined at 500°C for 2 hrs in a muffle furnace to convert the copper sulphate into copper oxide. Thus, copper oxide incorporated on laterite was obtained.

Chemical treatment of laterite by cationic surfactant

Ten grams of laterite sample was first conditioned with 1 M NaCl solution at room temperature, and afterwards washed with distilled water and dried out at 80°C for 4 hrs in a muffle furnace. Ten grams of laterite (Na-saturated) was mixed with 100 ml of N-Cetyl Trimethyl Ammonium Bromide of concentration 2 mmole/l. The suspension was shaken for 8 hrs at 150 rpm and 60°C in a shaking thermostat. The solution was filtered, and then the laterite sample was washed several times with de-ionised water and dried at 80°C for 4 hrs in a muffle furnace.

RESULT AND DISCUSSION

Adsorption capacity of different minerals

The equilibrium adsorption capacity of selected minerals was found at varying initial F^- concentration in the range of 2.5 to 25 mg/l at pH ~7 keeping adsorbent dosing constant (Fig. 1). Initially adsorption capacity increased with increase in fluoride concentration due to increase in availability of fluoride ions for adsorption. After that, no significant increase in adsorption capacity was observed due to saturation of adsorbent active sites. Adsorbent capacity was calculated as:

$$\text{Adsorption capacity} = \frac{(C_f - C_i) \times V_L}{W}$$

Where C_f = residual F^- concentration after equilibrium, C_i = initial F^- concentration, V_L volume of aqueous solution, W = mass of adsorbent

Laterite mineral with adoption capacity of 0.26 mg/g was reported with highest adsorption capacity over bauxite, calcite and hematite minerals and hence selected for further adsorption experiments. Sarkar et al. (2006) also reported a similar adsorption capacity for laterite, specifically 0.1955 mg/g at a pH of 7.5. Adsorption capacity of commercially available activated alumina and aeon was found as 1 and 1.15 mg/g, respectively. Maliyekkal et al. (2006) conducted an assessment of the adsorption capacity of activated alumina, observing a similar value of 1.08 mg/g at pH 7.

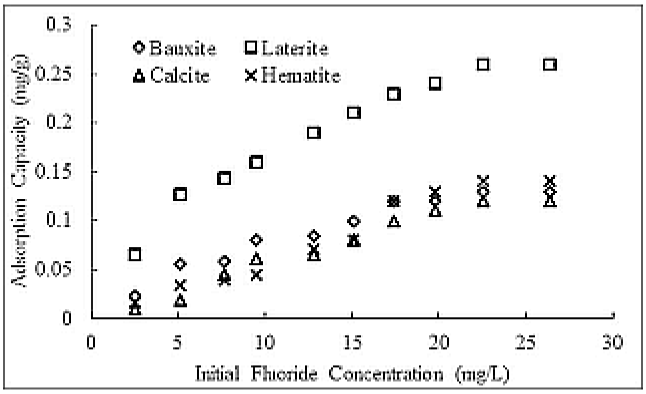

Figure 1. Adsorption capacity of pre-treated minerals at 105°C (optimum conditions - overflow of 72 mesh, Ph ~7, adsorbent dose = 1 g/100 ml, $[F^-]$ initial = 2.5–25 mg/l, 100 rpm at ambient temperature (27± 2°C))

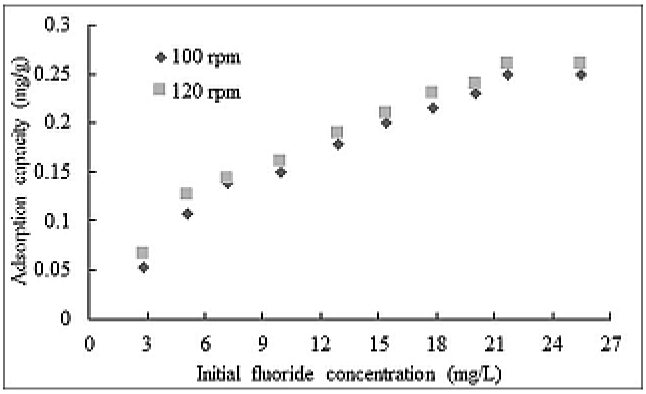

Figure 2. Effect of stirring speed on adsorption capacity of pre-treated laterite at 105°C (optimum conditions as in Figure 1)

Effect of stirring speed

To determine effect of mass transfer resistance on adsorption, experiments were performed for 100 and 150 rpm stirring speed (Fig. 2). Adsorption capacity was found to be almost same indicating adsorption is free from mass transfer resistance and is fully kinetically controlled. Hence 100 rpm was considered as optimum stirring speed for further experimentation.

Effect of adsorbent size

An adsorption experiments were performed for different size of adsorbent (over flow of 52, 72 and 100 mesh BSS screen i.e., 0.35, 0.25 and 0.15 mm, respectively) to evaluate optimum size of adsorbent. Increased adsorption capacities from 0.24 to 0.3 mg/g with decrease in adsorbent size were obtained due to increase in surface area and hence increase in adsorptive sites (Fig. 3). Though fine particles increase adsorption capacity but increases operational difficulties too like separation of adsorbent particles by filtration in batch experiments and clogging of adsorption bed in column operations. Thus, overflow of 72 mesh i.e. 0.25 mm adsorbent size was considered as optimum size for further

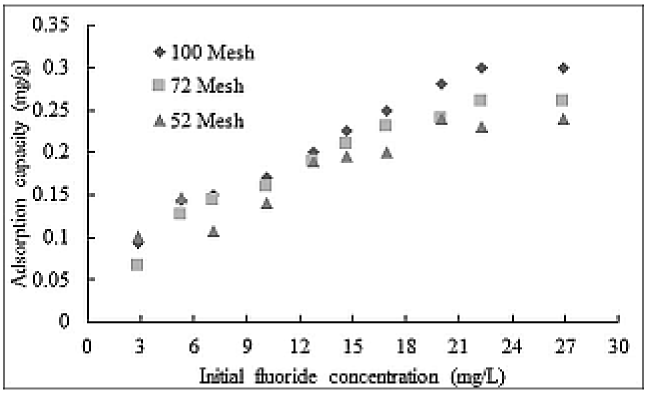

Figure 3. Effect of adsorbent size on adsorption capacity of pre-treated laterite at 105°C (optimum conditions as in Figure 1)

adsorption study.

Effect of thermal treatment

From the literature, it is noticed that surface area and hence adsorption capacity of adsorbent can be increased through thermal treatment. Thus, to evaluate the effect of thermal treatment on laterite adsorption capacity, laterite samples were thermally treated between 105 to 900°C. An increase in adsorption capacity was found from 0.26 mg/g at 105°C to 0.85 mg/g 600°C (Fig. 4). After 600°C, adsorption capacity was decreased to 0.76, 0.57 and 0.41 mg/g for 700, 800 and 900°C, respectively due to sintering of adsorbent creating blockage of available interior surface area for adsorption. Hence, for further optimization of adsorption parameter, thermally treated laterite samples at 600°C with increased surface area were considered for experimentation.

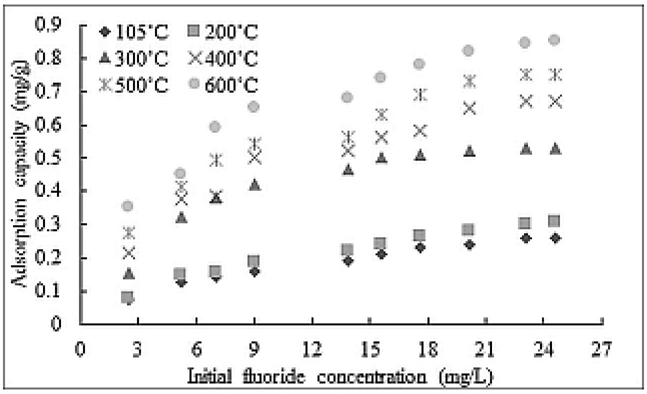

Figure 4. Effect of thermal treatment on adsorption capacity of laterite (optimum conditions as in Figure 1)

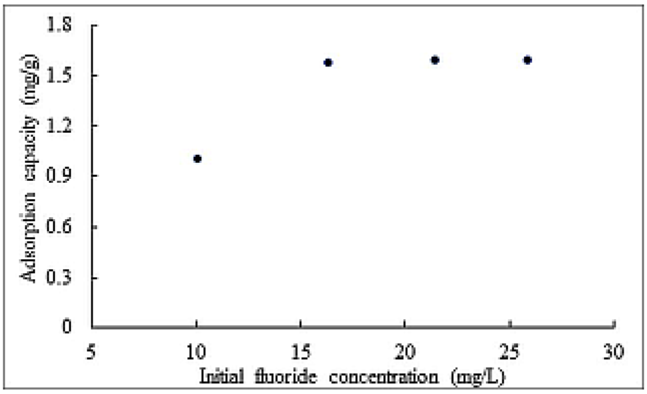

Figure 5. Adsorption capacity of copper oxide coated laterite (optimum conditions as in Figure 1)

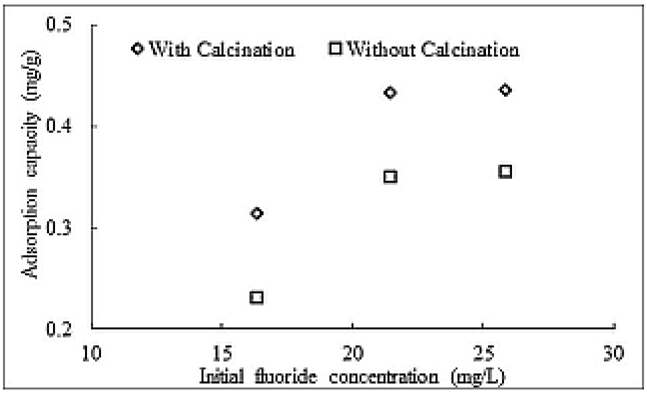

Figure 6. Adsorption capacity of N- Cetyl Trimethyl Ammonium Bromide modified laterite (optimum conditions as in Figure 1)

Effect of chemical treatment

Initially surface modification was performed at high concentration of $CuSO_4$ (0.05 M) and N-Cetyl Trimethyl Ammonium Bromide (2 mmole/l). Adsorption Capacity of $CuSO_4$ treated laterite was recorded four times more than that of surfactant treated laterite (Figs. 5, 6). Hence, $CuSO_4$ treatment on laterite was chosen for optimization study. The $CuSO_4$ concentrations, used for laterite surface modification, were varied from 0.005–0.05 M to optimize chemical dosing. Adsorption experiments were conducted for each of surface modified laterite. Maximum adsorption capacity of 1.905 mg/g was recorded for 0.01 M concentration of $CuSO_4$ (Fig. 7).

Adsorption isotherm

Adsorption isotherm is one of the most significant tools to predict the adsorption capacity of the adsorbent and the adsorption mechanism. Isothermal

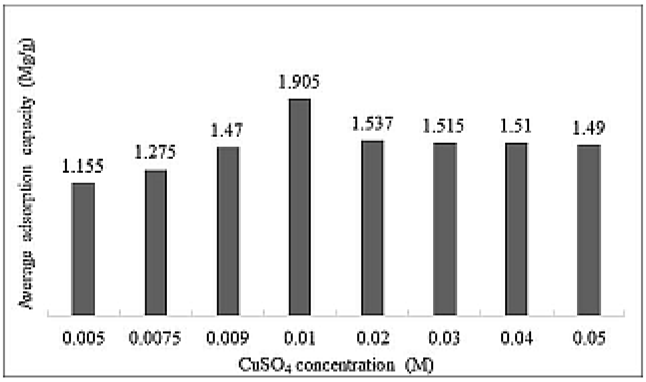

Figure 7. Effect of $CuSO_4$ concentrations on adsorption capacity of laterite (optimum conditions as in Figure 1)

studies were carried out for the adsorption of fluoride onto surface modified laterite at optimized conditions. The adsorption data were examined using two isotherms, namely, Langmuir and Freundlich isotherms.

Langmuir Isotherm: $\frac{1}{q_e} = \left(\frac{1}{K\, q_{max}} \times \frac{1}{C_e}\right) + \left(\frac{1}{q_{max}}\right)$

Freundlich Isotherm: $\log q_e = \log K_f + \left(\frac{1}{n} \times \log C_e\right)$

Where, q_{max} = adsorption capacity, K= Slope, K_f= Freundlich constant, n = Constant relating to adsorption intensity

Figures 8 and 9 represents the Langmuir and Freundlich plots from the experimental data from which isotherm parameters were obtained (Table 1). Our results suggest Freundlich isotherm to be best suited to the fluoride adsorption. The value of n lied between 1 to 10 representing favourable conditions for multilayer adsorption.

Laterite characterization

Pre-treated, calcined and $CuSO_4$ treated laterite morphology, was studied using SEM and micrographs (Figs. 10, 11, 12). While, the micrograph of pre-treated laterite indicated that laterite surface had a porous surface, calcined laterite showed increased surface area. Similarly, the $CuSO_4$ treated laterite also showed change in surface are which is due to chemical loading. It is mainly because of copper oxide being adsorbed on the external surface of laterite.

Surface area and pore volume of pre-treated, calcite and copper oxide loaded laterite were determined using the BET analysis (Table 2). Surface area and pore volume of the pre-treated laterite were 16.796 m²/g and 0.038 cc/g, respectively. An increase in surface area and pore volume for calcined laterite was noticed due to loss of internal moisture. Surface area and pore volume of copper oxide loaded laterite were recorded as 13.137 m²/g and 0.030 cc/g, respectively. The surface area and pore volume of copper oxide loaded laterite decreased due to chemical treatment. Due to chemical treatment, some of the main channels of pre-treated laterite became obstructed by copper oxide loading; therefore, the diffusion of N_2 into these channels was impeded, and resulted in decreasing the specific surface area and pore volume. The half pore width of the natural pumice after copper oxide loaded laterite was increased, perhaps the result of the blockage of the smallest pore diameters with loading; and consequently, increased its half pore width.

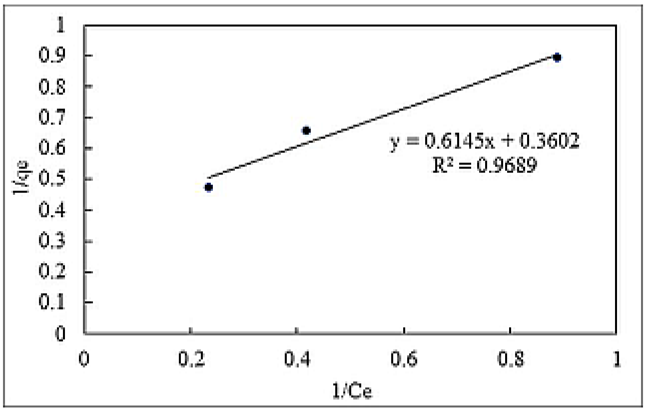

Figure 8. Langmuir isotherm modelling for adsorption studies of fluoride onto $CuSO_4$ treated laterite system at optimized conditions

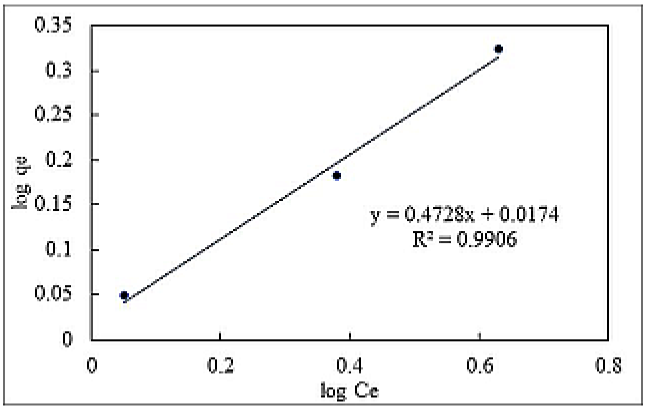

Figure 9. Freundlich isotherm modelling for adsorption studies of fluoride onto $CuSO_4$ treated laterite system at optimized conditions

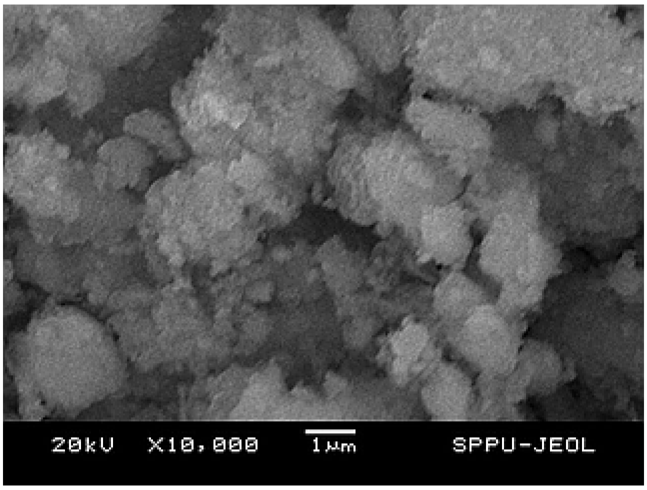

Figure 10. SEM image of pre-treated laterite

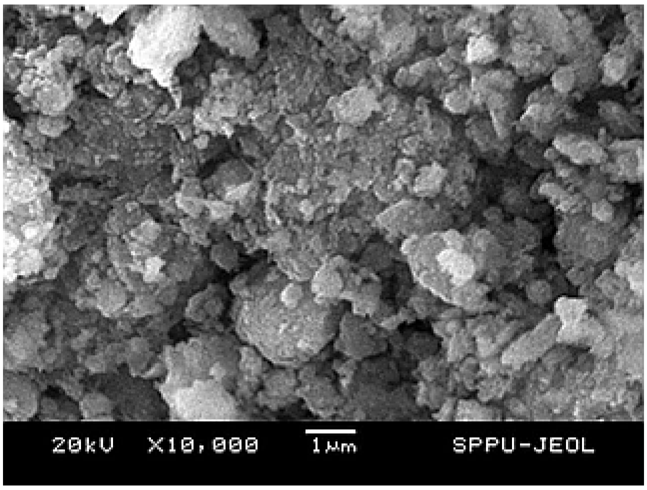

Figure 11. SEM image of calcined laterite

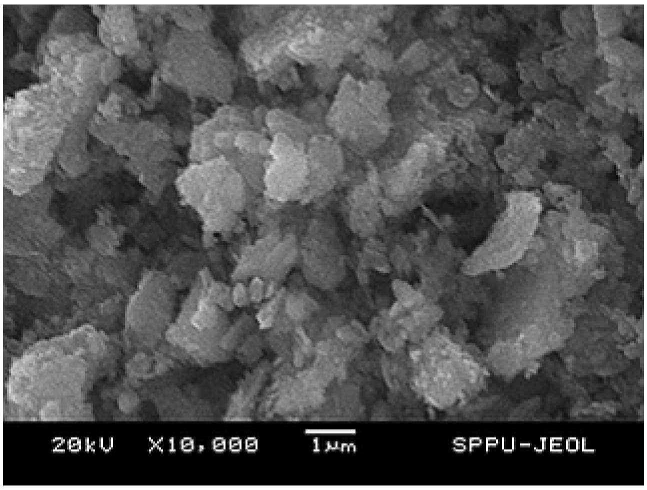

Figure 12. SEM Image of copper oxide loaded laterite ($CuSO_4$ treated laterite)

Table 1. Isothermal parameters for adsorption study of fluoride $CuSO_4$ treated laterite system at optimized conditions

Langmuir isotherm	**Freundlich isotherm**
$R^2 = 0.9688$	$R^2 = 0.9906$
$q_{max} = 2.7762$	$1/n = 0.472$
$K = 0.5861$	$K_f = 1.0409$

Table 2. BET analysis of pre-treated, calcite and $CuSO_4$ treated laterite

	Pre-treated laterite	**Calcined laterite**	**CuO loaded laterite**
Surface area (m^2/g)	16.796	50.824	13.137
Pore volume (cc/g)	0.038	0.148	0.030
Half pore width (Mode (dLog))	15.149 Å	15.149 Å	18.137 Å

CONCLUSION

In present study, Laterite, Bauxite, Hematite and Calcite minerals, ores of iron, aluminium and calcium respectively, are considered for F^- ion adsorption from water at 7 pH and atmospheric temperature. Laterite mineral is selected for further fluoride removal experiments due to its highest adsorption capacity as compared to other selected minerals. Different adsorption parameters like effect of stirring speed, adsorbent size and thermal treatment on adsorbent capacity of laterite were studied. In the present study with increasing stirring speed, adsorption capacity was found to be almost same indicating adsorption is free from mass transfer resistance and is fully kinetically controlled. Increase in adsorption capacity with decrease in adsorbent size was noticed. But to avoid operational difficulties like clogging of bed and filtration media, moderate size of adsorbent was selected for further adsorption experiment. An increase in adsorption capacity up to certain rise in thermal temperature due to increase in surface area was noticed. At high temperature, decreased adsorption capacity was calculate due to sintering of adsorbent. Hence optimum temperature, 600°C was selected for thermal treatment of adsorbent.

Raw laterite was successfully modified with copper oxide loaded laterite using copper sulphate solution. Optimum loading was recorded for 0.01 M copper sulphate solution with laterite of overflow 72 mesh i.e. 0.25 mm. Adsorption capacity had been successfully increased from 0.26 mg/g for pre-treated laterite to 0.85 mg/g for calcined laterite to 1.905 mg/g for copper oxide loaded laterite. Eight-fold increase in adsorption capacity was obtained with surface modified (copper oxide loaded) laterite over raw laterite and higher than commercially available adsorbents activated alumina and aeon. Result revealed that copper oxide loaded laterite is a potentially strong adsorbent for F^- removal at room temperature with neutral pH. Adsorption experiments are supported by Freundlich isotherm indicating physical multilayer adsorption with electrostatic force of attraction.

Authors' contributions: All authors contributed equally.

Conflict of interest: Authors declare no conflict of interest.

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