GSC Advanced Research and Reviews
eISSN: 2582-4597 CODEN (USA): GARRC2
Cross Ref DOI: 10.30574/gscarr
Journal homepage: https://gsconlinepress.com/journals/gscarr/

(RESEARCH ARTICLE)

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Defluoridation studies of calcium and magnesium coating on activated alumina granules prepared by sol gel method

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GSC Advanced Research and Reviews, 2024, 21(02), 504-512

Publication history: Received on 02 October 2023; revised on 17 November 2024; accepted on 19 November 2024

Article DOI: https://doi.org/10.30574/gscarr.2024.21.2.0412

Abstract

The contamination of fluoride in ground water has become global issue which has developed major threat to human health worldwide. Adsorption technique for water defluoridation is widely used method due to its greater accessibility and lower cost. Activated alumina is excellent adsorbent for fluoride removal however it has certain disadvantages like narrow operating pH range, formation of toxic fluoride complexes and metal leaching. To overcome these issues we have prepared calcium and magnesium coated activated alumina granules of size nearly 3 mm by hydrolysis of aluminum sulphate which is simple, cheap and economic method.The prepared granules were characterized and identified by XRD, FT-IR and SEM technique. The XRD, FT-IR and SEM micrographs confirms the formation of homogeneous and porous γ alumina phase with average particle size of around 45 nm. The fluoride removal capacity of the granules was investigated by column studies using freshly prepared fluoride stock solution. The calcium magnesium coated alumina granules shows decreased removal capacity than pure alumina granules however no formation of toxic aluminium complexes in the treated water were observed.

Keywords: Calcium Magnesium Coating; Defluoridation; Activated Alumina; Hydrolysis Method

1. Introduction

The past few decade'swater crises have become one of the major problems in urban as well as rural areas. There are many reasons for the degradation of water quality which includes population growth, industrialization in urban area, urbanization and unskilled utilization of water resources [1]. Many countries like United States, China, South Africa, Tanzania, Kenya, Ethiopia, Turkey, Israel, Indonesia, Finland, Ghana, Argentina,Brazil, Mexico, Canada, Germany, Pakistan, etc arefacing water toxicity problemand developing strategies to tackle this. [2-13]. Thequality of the water is affected by lot of factors which may be physical, individual,chemical, hydrological, and biological etc. Usually, dissolved water contaminants are present in groundwater than in surface water which is due to greater interaction of ground water with various materials in geologic strata [14]. The elements like fluoride, chromium, cadmium, lead, arsenic, etc are hazardous when they are present beyond safe limit in ground as well as surface water [15].

The presence of excess fluoride in drinking water causes several diseases to human health depending on its concentration levels. A small concentration of fluoride is beneficial for tooth enamel. When exposure of fluoride containing drinking water is more, it causes dental and skeletal fluorosis. Therefore, it is essential to maintain proper level of fluoride in drinking water as per regulatory standards and guidelines. The World Health Organization (WHO) guidelines suggest the level of fluoride in drinking water around 1.5 mg/L[7-8]. According to the Bureau of Indian Standards (BIS), the permissible upper limit of fluoride in drinking water in India should not go beyond 1.0 mg/L. The water containing excess amount of fluoride leads to large amount of hydroxyapatite converting into fluorapatite which

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results in denser teeth and bone, harder and more brittle and gives rise a disease called dental fluorosis [13]. When the fluoride concentration in water exceeds 3.0 mg/L, dental fluorosis results in conversion into skeletal fluorosis [16]. This also further associated with decreased birth rates, increased rates of kidney stones,Alzheimer syndrome, impaired thyroid function and lower intelligence in children, thyroid disorder, neurological damage. The higher concentrations of fluoride can also responsible to interfere with DNA synthesis, proteins, carbohydrates, lipids, vitamin and mineral metabolism [17].

There are many methods to treat fluoride contaminated water like ion exchange, coagulation, membrane filtration, chemical precipitation, Nalagonga techniques, etc. All these methods require high installation and maintenance cost. Moreover, it also requires trained operator which also adds in filtration cost. The adsorption method has attracted many researchers particularly for fluoride removal due to its simple arrangement, cost effectiveness and its feasibility in remote areas. [18] Various adsorbent materials can be used as an adsorbent which include activated carbon, activated alumina, rice husk, red mud, CNT, zeolite, hydroxyapatite, chitosan, magnesia, quick lime and many more. SubhashiniGhorai et al (2004) reported remarkably excellent fluoride removal capacity by using activated alumina. The adsorption isotherm showed close agreement with Langmuir equation and isotherm constants [19]. Chen et.al. synthesized Fe–Al–Cetrimetal hydroxide adsorbent for fluoride removal from drinking water and studied removal efficiency [20]. Aluminium hydroxide coated rice husk ash (RHA) was examined by Vivek and Kalyan. The coating of rice husk was carried out using aluminium salt solution of 0.6 N and sodium hydroxide solution [21]. M. Changmai (2017) et al have studied removal of fluoride using aluminium oxide nanoparticles which is synthesized in the presence of oxidizing agents H_2SO_4, $KMnO_4$ and $K_2Cr_2O_7$[22].C.M.VivekVardhan et al have developed low-cost adsorbent Lanthanum Impregnated Pumice (LIP), to study the effect of Lanthanum and Pumice on removal of fluoride from water[23].

Out of various adsorbents activated alumina shows better removal capacity over other adsorbents. However, activated alumina favors narrow operating pH range, formation of toxic aluminium fluoride complexes, and leaching of aluminium metal into treated water. To overcome these issues, in this present work we have prepared activated alumina granules by hydrolysis method and coated with calcium and magnesium. These coated granules were examined for fluoride removal. Calcium and magnesium are easily available elements and has strong affinity towards fluoride. The calcium and magnesium coating not only prevents aluminium leaching into the treated water but also contribute to daily Ca and Mg intake.

2. Material and method

2.1. Material

For the preparation of calcium and magnesium amended activated alumina granules, the chemicals used are aluminum sulphate (AR grade), calcium chloride (AR) ($CaCl_2 \cdot 2H_2O$), magnesium chloride (AR) ($MgCl_2 \cdot 6H_2O$), sodium hydroxide (AR) (NaOH), double distilled water. All the chemicals utilized in this study were of analytical reagent (AR) grade and were obtained from M/s Merck India Ltd.

2.2. Synthesis process

In order to prepare alumina granules, first alumina sol was prepared by hydrolysis of aluminum sulphate. The aluminium sulphate solution was freshly prepared by dissolving measured quantity of it in double distilled water. To this solution 0.1 M sodium hydroxide (NaOH) is added drop-wise to form white precipitate. During addition of NaOH solution, the pH was maintained neutral till complete precipitation. This turbid solution was kept at constant temperature 70˚C in water bath for at least 6 to 7 hours until the mixture reached the point of gel formation. This gel was allowed to settle overnight and next day supernatant liquid was then discarded carefully or filtered with the help of filter paper. This sol was washed with warm water two to three times, to remove excess sulphate ions. This precipitate was ultrasonically dispersed by adding few drops HNO_3 and transferred to dropper. The sol droplets were fell into liquid bath containing ammonia and paraffin oil to form granules as shown in figure 1. The granules were dried at 30 to 40˚C in hot air oven to remove excess content of water. These granules were sintered into the muffle furnace for at least 3 hours at 600˚C temperature. For calcium coating, the sintered alumina granules were dipped into calcium chloride solution for 1 hour maintaining pH 9 and dried at 100˚C followed by sintering at 600˚C for another 4 hours. For magnesium coating, calcium coated granules was dipped into magnesium chloride solution for 1 hour at constant pH 12 and dried at 100˚C with sintering at 600˚C for 4 hours. The fluoride removal capacity of these granules was studied by up flow column study using domestic candle type filter by filling hollow column by granules and then plugging it with cotton. The test solution with known concentration was prepared by dissolving sodium fluoride in distilled water(10, 20 and 30 ppm). This test solution was passed through pure alumina and coated alumina column in upward direction

in order to achieve uniform flow of 100 ml per 15 minutes. The concentration of fluoride in treated water was measured and amount of fluoride removed during column study was estimated. This process was continued for number of cycles until the adsorbent column gets exhausted.

Fig (a)

Fig (b)

Fig (c)

Figure 1 (a), (b), (c), shows synthesis part and AA granules

3. Result and discussion

The crystalline structure and phase of the granules was investigated by wideanglepowder X-Ray diffractometer using Cu- Kα source. All the scan were recorded in the 2θ region of 0- 80˚at a scan rate of 0.020 per second. Fig. 1 shows the XRD pattern of the sample prepared via hydrolysis method and sintered at 600˚C.

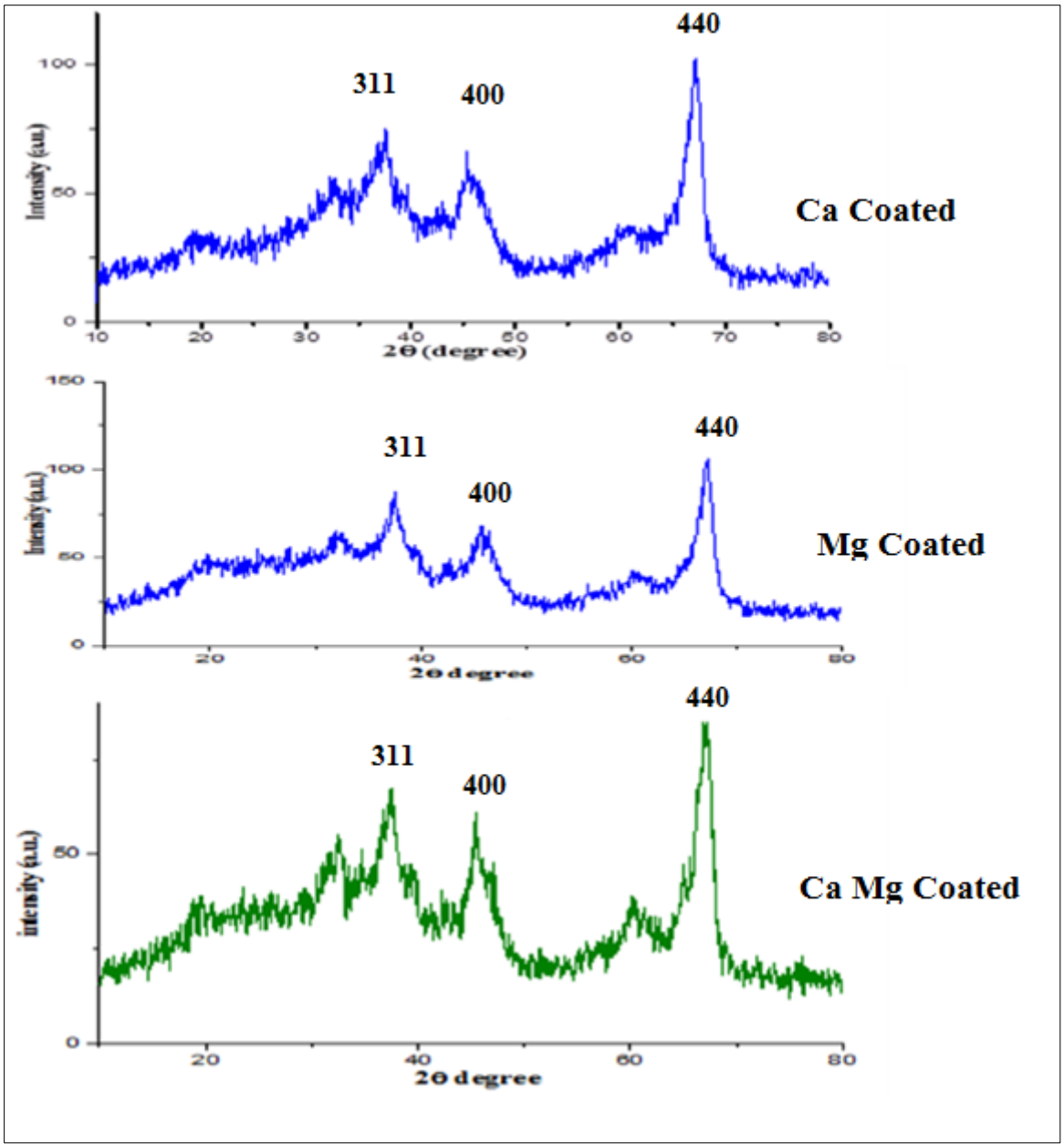

Figure 2 XRD diffraction of (i) Ca coated (ii) Mg coated and (iii) Ca Mg coated activated alumina granules

Figure 2 shows the XRD diffraction peaks corresponding to oxide phase only. The peaks are relatively broader showing weak crystalline nature and amorphous γ- Al_2O_3 phase. This X-ray diffraction pattern were compared with standard JCPDS data, 100% peak intensity observedat 66.90˚, 2θ value which closely matches with reference data [26]. The particle size of laboratory prepared activated alumina granules were calculated from Debye-Scherrer formula and was found to be 45 nm. The XRD pattern of the prepared granules closely matches with JCPDS file no. 20-063 which is corresponding to γ- Al_2O_3 phase.The prepared alumina granule samples also display distinct diffraction peaks for γ - Al_2O_3 (ICDD JCPDS No. 98-000-0059; a spinel-type structure; space group Fd3m) [24-25], with all γ -Al2O3 nanoparticles showing similarity in relative peak intensities. The γ -alumina sample obtained through this method shows weak crystallinity which might due to peak broadening effect observed in nano-materials. The average crystallite size of 45 nm calculated from Scherrer peak broadening equation, which lies within the range of nano dimension powder. At the certain elevated temperature of 600˚C, some desorption and dehydration of hydroxyl groups present on the surface lead to the formation of γ-alumina which is based on distorted spinel structure [27]. The obtained peaks were analyzed by curve fitting method; it was observed that the peaks exhibit broad and diffuse profiles which indicate presence of small crystalline grains with small compositional fluctuations. This is also consistent with the location of the Al^{3+}ions either by the tetrahedral or octahedral sites within the spinel structure.[28]

To study surface morphology of the prepared granules, SEM analysis was performed and presented in fig. 3. SEM micrographs of pure activated alumina (AA) granules prepared by hydrolysis method, shows uniform flake, plate or leaves like structure. The compound forms agglomerated particle when it was sintered at some elevated temperature of 600°C. The matrix consists of Al_2O_3 with an average grain size of about 50 nm and which is in accordance with the value calculated from Scherer formula (XRD studies). It can also be observed from SEM micrograph that the Al_2O_3 grains are connected via sintering necks.

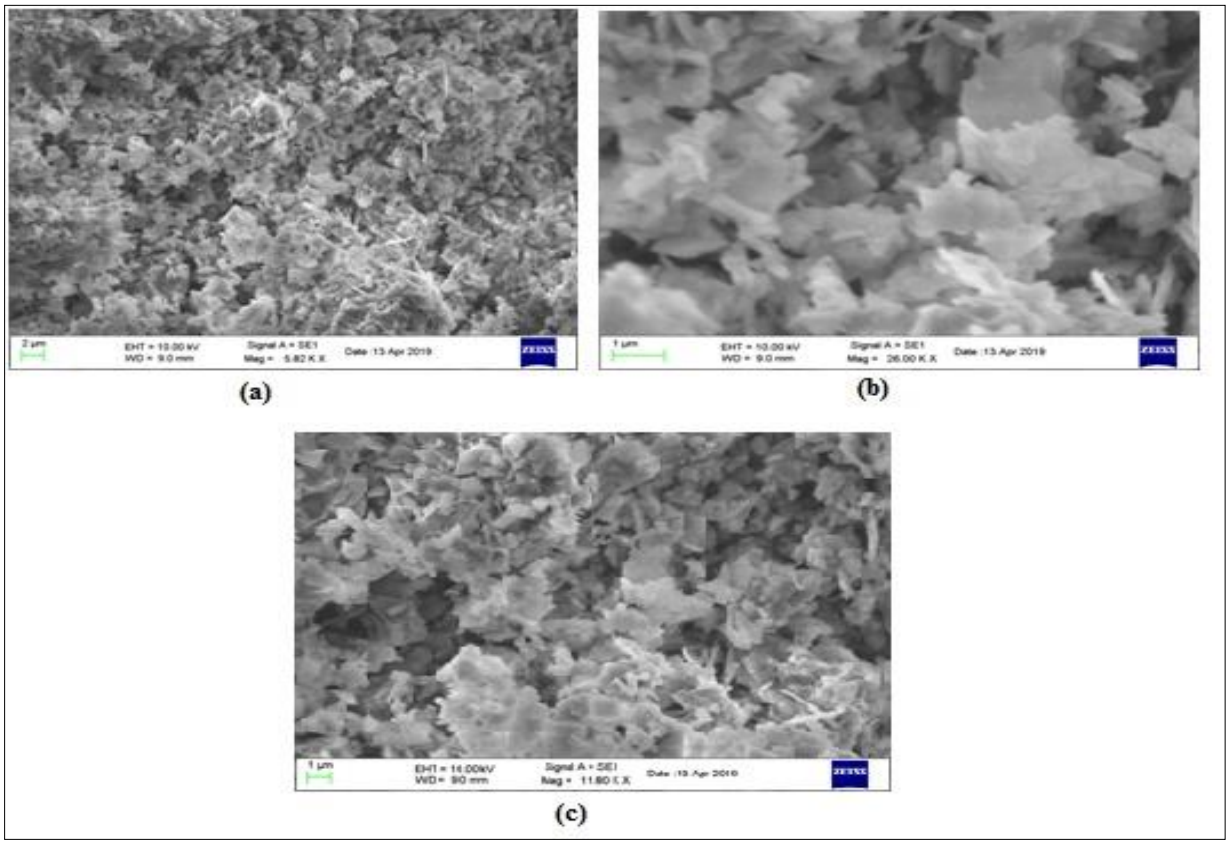

Figure 3 (a), (b), (c) show same image of laboratory synthesized activated alumina (AA)

An infrared spectrometer (IFS66, Bruker) was used to record IR-reflectance spectra of alumina-based ceramics. The spectra were measured from 500 to 3500 cm^{-1} with a spectral resolution of 2 cm^{-1}. The angle of incident was 20° and the light was either parallel or perpendicular polarized. Polished glasses and glass ceramics were used for the measurements to maximize the specular reflectance. The FTIR shows the laboratory synthesized material pre fluoride treated AA, MCAA, CCAA, MCCAA adsorbent calcinated at 600°C shows a series of broad band spectrum. As the calcinations temperature increases the absorption peaks becomes flat which is due to evaporation of some organic liquids and water which has been shown in the figure. The band observed at 545 cm−1 represents aluminum ions located at octahedral and tetrahedral environments. These results are in agreement with the FTIR spectrum of γ -alumina as reported elsewhere. The major absorption peak of Aluminum sulphate is obtained at wave number 1088 cm^{-1}. The peak obtained at 1230 cm^{-1} attributed to vibration of sodium sulphate group bending bands. The magnesium peak was observed at the wave number of 1600 cm^{-1}. The peaks seem to be broadening at 3450 cm^{-1} which is due to vibration of OH- stretching bond. Also, the peaks between 800 and 612 cm^{-1} correspond to the Al-O vibration. Doubly broad band peak of chlorine mode of vibration was observed at particular wave number at 880.25 cm^{-1}. The sharp narrow peak indicated the presence of magnesium at wave number 480 cm^{-1}. [29-31]

From Fig. 4, the band observed at wave number 1055 cm−1was attributed to vibrations of Al-O stretching bond whereas the peak Fig. 3. FT-IR spectra of alumina granules.observed at 1630 cm−1can be due to hydroxyl group (-OH) which shows the existence of physically adsorbed water content in the sample. The band observed at 545 cm^{-1} represents aluminum ions located at octahedral and tetrahedral environments. These results are in agreement with the FTIR spectrum of γ -alumina as reported elsewhere. The band between 1398 cm−1 was observed, indicating that the CO2 molecules chemically adsorbedwere not eliminated during synthesis process. This band would disappear when the sample is heated at desired elevated temperature.

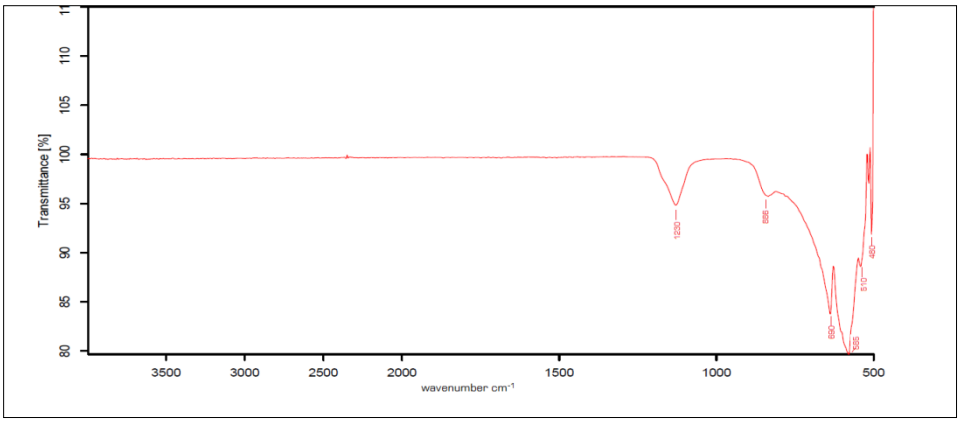

Figure 4 (a) FTIR AA

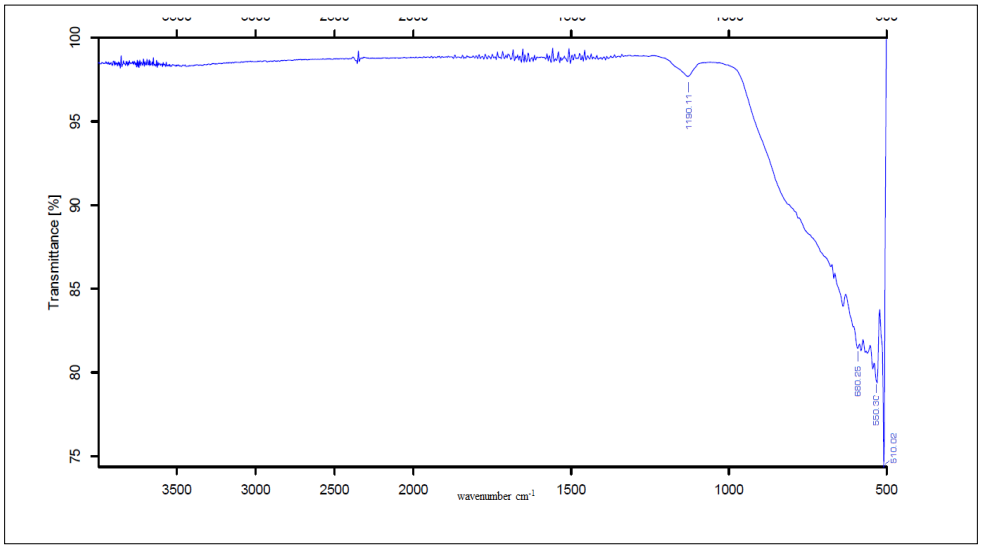

Figure 4 (b) Calcium coated activated alumina (CCAA)

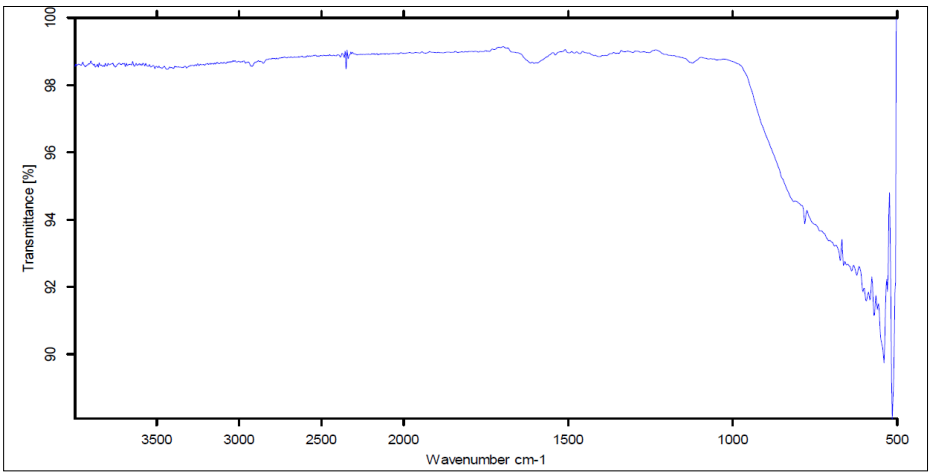

Figure 4 (c) magnesium Calcium coated activated alumina (MCCAA)

The fluoride removal capacity of the activated alumina and Ca and Mg amended alumina was studied using ionic conductivity method. Prior to study, the test solution was prepared using sodium fluoride with fluoride content 10, 20, and 30 ppm called initial concentration. The known test solution was prepared by dissolving sodium fluoride in distilled water in different concentrations (10, 20 and 30 ppm). The test solution was passed through alumina column in upward

direction in order to achieve uniform flow. The flow rate was maintained at 100 ml per 15 minutes. The results are expressed in table 1 and figure 5.

Table 1 Fluoride removal efficiency of AA

sample	Initial concentration (ppm)	Final Fluoride (ppm)
AA10	10ppm	2.4 ppm (76%)
AA20	20ppm	2.55ppm (87.25%)
AA30	30ppm	2.601ppm (91.33%)

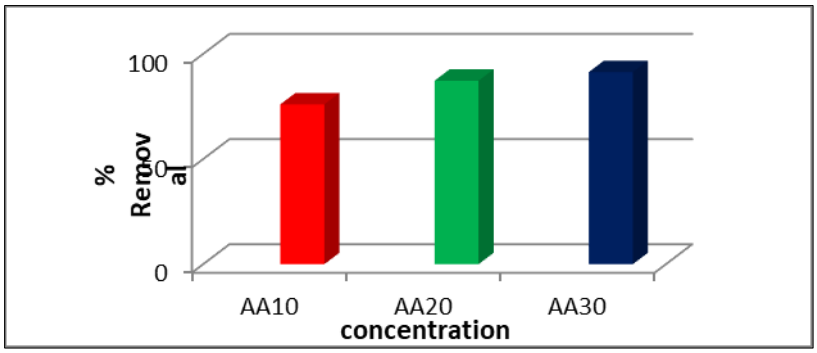

Figure 5 Fluoride removal capacity of pure AA

The regeneration studies of exhausted calcium, magnesium amended activated alumina were conducted using NaOH (sodium hydroxide). It can be seen from regeneration study that the exhausted alumina can be regenerated in high alkaline environment. The desorption percentage was 75% and 88% for 0.1 M and 0.5 M NaOH respectively after 8 h of operation. The increase in the concentration of NaOH and time of operation leads to enhance the desorption percentage. There are many studies on the removal of fluoride using various adsorbents, but there are hardly few studies on the reusability of adsorbant. In the present study we have also observed the defluoridation capacity of activated alumina for ten cycles and results are shown in figure 6. The advantage of using AA in granular form is its stability after many usage hence it shows nearly same capacity of fluoride removal even after ten cycles of usage.

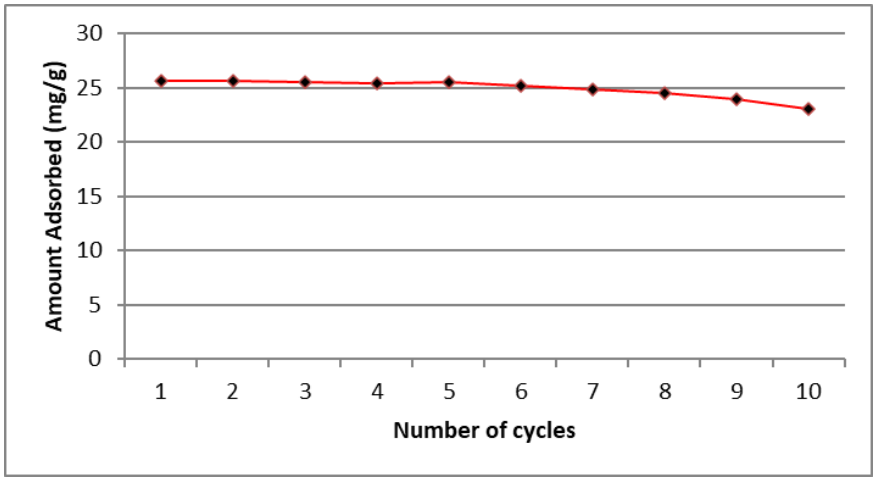

Figure 6 Number of cycles versus fluoride adsorbed by activated alumina

4. Conclusion

In this study we have successfully synthesized activated alumina (AA) granules by sol gel method using aluminum sulphate and sodium hydroxide and treated at 650 °C. This activated alumina granules were coated with calcium and magnesium and formed magnesium coated activated alumina (MCAA), calcium coated activated alumina (CCAA) and magnesium-calcium coated activated alumina (MCAA). The granules were prepared by simple technique with the help of syringe and show good strength which is suitable for handling water pressure. XRD confirms the formation of amorphous γ alumina with particle size of 45 nm calculated from Scherrer formula. The laboratory synthesized activated alumina coated with Calcium, Magnesium and Calcium-Magnesium shows similar peaks similar to that of uncoated activated alumina. In FTIR study the broad-spectrum peak of aluminum sulphate was observed at a particular wave number 1088 cm^{-1}. The peak obtained at 1230 cm^{-1} attributed to vibration of sodium sulphate group bending bands. The magnesium peak was observed at 1600 cm^{-1} whereas the peak observed at 3450 cm^{-1} is due to vibration of OH- stretching bond. Also, the peaks between 800 and 612 cm^{-1} correspond to the Al-O vibration. The sharp narrow peak at wave number 480 cm^{-1} indicates the presence of magnesium. In SEM study the host matrix consists of Al_2O_3 with a average grain size of about 50 nm shows good agreement with the average particle size calculated from the XRD. The Al_2O_3 grains are connected via sintering necks. The SEM image of the pure alumina shows uniform homogeneous flake or plates like structure whereas Mg and Ca coated alumina shows amorphous and weak crystalline structure indicating the deposition of Mg and Ca on the surface of alumina making it more porous as required for the fluoride adsorption. The main disadvantage of activated alumina is its amphoteric nature and narrow favorable pH range available i.e. pH 5.5 to 6.5 for fluoride removal. Therefore, pre-treatment of feed water is required for neutral or basic feed. Presence of aluminum in dissolved and colloidal forms has been reported in water treated with aluminum-based adsorbents such as alumina and alum. Moreover, the regeneration process of exhausted AA uses corrosive acids and bases, which lead to release of aluminum fluoride complexes and solid alumina waste that are toxic in nature. The calcium and magnesium coated activated alumina shows better defluoridation performance over wide pH range. The fluoride adsorption capacity of activated alumina found to slight decrease with the amendment of calcium and magnesium due to deposition of calcium and magnesium ions on the active surface of activated alumina. The calcium and magnesium amended activated alumina prevents formation of toxic aluminum complexes. It also shows better regeneration even after ten cycles of usage. In future it would be possible to enhance adsorption capacity of activated alumina by coating it with different material. The combination of calcium and magnesium on to the activated alumina surface was successful with the formation of calcium and magnesium complexes with aluminum sulphate surface thereby increasing the reactivity of the adsorbent towards fluoride which is simple, cheap and economic method.

Compliance with ethical standards

Acknowledgments

The authors RM Belekar and AS Boche would like to thank Science and Engineering Research Board (SERB), Department of Science and Technology (DST) of the Government of India (GOI) for financial support. Grant Number: EEQ/2022/000228.

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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