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1 **A facile synthesis of metal ion-imprinted graphene oxide/alginate hybrid biopolymeric**
2 **beads for enhanced fluoride sorption**

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24 **ABSTRACT**

25 The enhanced surface properties of graphene oxide (GO) illustrate its vital role in
26 environmental remediation. However it is difficult to use it in column studies, as it causes
27 pressure drop during field applications. To overwhelm its drawbacks and to improve its
28 adsorption feature, GO was synthesized in an usable bead form by interspersing GO in alginate
29 (Alg) polymatrix and cross-linked with La(III) ion (GOAlgLa). The synthesized GOAlgLa
30 composite beads not only displays good field application but also demonstrate extremely
31 enhanced defluoridation capacity (DC) than GO. The DC of GOAlgLa composite beads and GO
32 was found to be 6617 and 2438 mgF⁻ kg⁻¹ respectively. To find the effect of different influencing
33 parameters like pH, contact time, competitor co-anions, temperature and initial fluoride
34 concentration studies were conducted in batch mode. The sorbents were analyzed using various
35 characterization techniques like FTIR, TEM, SEM, EDAX, and Raman analysis. The
36 characteristics of the sorption process were investigated using Freundlich, Langmuir, and D-R
37 isotherms. The value of thermodynamic parameters indicates that fluoride sorption onto
38 GOAlgLa composite beads was endothermic and spontaneous in nature. GOAlgLa composite
39 beads also reveal a good regenerability over repeated adsorption/desorption process. The
40 applicability of hybrid beads to field water sample, indicate its adaptable nature at field
41 conditions.

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48 1. INTRODUCTION

49 The removal of toxic ions from the water has great concern worldwide, due to their
50 adverse effect on human beings and on the environment. Fluoride causes adverse effects to
51 human health when its concentration exceeds $> 1.5 \text{ mg L}^{-1}$ in drinking water. The excess fluoride
52 level in drinking water leads to different forms of fluorosis.¹ One of the foremost sources of
53 fluoride ingested by the human being is drinking water. The major source of fluoride are fluoride
54 bearing rocks/minerals and various industrial activities. The mineral such as fluorite, cryolite,
55 ralstonite, micas, etc., that contain fluoride are prevalent components of the sediments.² In
56 developing countries, ground water is a deliberate requirement for drinking, cooking, domestic
57 purposes, etc., but unfortunately the fluoride concentrations of it is more than 1.5 mg L^{-1} in
58 several places of India and other foreign countries. Hence, it is necessary to provide water with
59 safe fluoride levels to the common people, devouring excess fluoride contaminated water.

60 Numerous fluoride remediation technologies, including precipitation, ion-exchange,
61 electrocoagulation, electrodialysis, nanofiltration, reverse osmosis, and adsorption³⁻⁹ have been
62 developed. Amongst them adsorption is believed as a simple, efficient and universal option than
63 the other reported techniques. The recycling of the adsorbent and the low generation of residues
64 in this technique are the more advantages than the other fluoride removal methods.¹⁰⁻¹²
65 Researchers all over the world paid plentiful efforts to develop a novel and efficient adsorbent
66 for the removal of fluoride from the aqueous solution.

67 Graphene oxide has much attention in recent years and shows promising adsorption
68 performance towards toxic ions owing its huge surface area, copious surface functional groups
69 (hydroxyl and carboxyl groups), incredible dispersible properties in water, and their easy
70 modification.¹³⁻¹⁹ Even though GO possesses good adsorption efficiency for the removal of toxic

71 ions, the application of GO in column studies is restricted due to its powder nature, brittleness,
72 and poor mechanical strength. To overcome such industrial blockage polymer assisted GO
73 composite beads were prepared. The synthesized polymeric composite beads have unique
74 properties like hardness, inflexibility, and mold shrinkage which helps to develop the modern
75 technology.²⁰⁻²²

76 Recently researchers have paid more attention towards the biosorption process for
77 environmental remediation because of its eco-friendly, non-toxic, biofunctional, biocompatible,
78 and biodegradable properties.²³⁻²⁵ Alginate is a biopolymer and it is collection of two different
79 monomers viz., (1→4) β-D-mannuronate and (1→4) α-L-guluronate and it is obtained from
80 brown seaweeds. Alginate assisted composite adsorbents were extensively studied for toxic ions
81 removal due its non-toxic, biodegradable and biocompatible nature.²⁶⁻³⁰ It possesses a very good
82 affinity towards different metal ions to form ionotropic alginate metal complex beads. But,
83 divalent cations cross-linked alginate composites beads are unstable in acidic medium because
84 the divalent metal ions can easily replaced by H⁺ ions.³¹ To improve the adsorption capacity,
85 reusability, and solidity, high valence metal ions (trivalent, tetravalent, etc..) is utilized as cross-
86 linker to develop the hybrid beads. In recent time, the development of new adsorbents with
87 selectivity and high performance towards fluoride was done by incorporation of high valence
88 metal ions into the adsorbent materials.³²⁻⁴⁰ Hence, we have synthesized La(III) ion cross-linked
89 alginate/graphene oxide composite beads for the sorption of fluoride.

90 The present investigation aimed to synthesis economical, efficient, and eco-friendly
91 composite beads by interspersing GO in Alg polymeric matrix and cross-linked with La(III) ion.
92 The developed GOAlgLa composite beads were effectively utilized for fluoride sorption. To find
93 the effect of different influencing parameters like competitor co-anions, pH, contact time, initial

94 fluoride concentration, and temperature the batch mode were carried out. A comparative study
95 was carried out for GO and GOAlgLa composite beads to estimate the defluoridation capacity.
96 The experimental results were fitted with various isotherm and thermodynamic parameters. The
97 effective utilization of GOAlgLa composite beads to the field water sample was done at nearby
98 fluoride rife area in Dindigul district of Tamilnadu.

99 **2. EXPERIMENTAL SECTION**

100 **2.1. Materials**

101 Sodium alginate was purchased from Himedia (India). Graphite flakes was purchased
102 from Central Drug House (India). Conc. H_2SO_4 , NaNO_3 , KMnO_4 , H_2O_2 , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$,
103 $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and all other chemicals were purchased from Merck (India) and used as such
104 without further purification. A fluoride solution containing 1000 mgL^{-1} was prepared by
105 dissolving 2.21 g of NaF (AR grade) in 1000 mL of double distilled water. The working solution
106 of 20 mg L^{-1} for batch fluoride sorption process was then prepared by appropriate dilution of the
107 stock solution.

108 **2.2. Synthesis of GO**

109 Graphene oxide was synthesized from natural graphite powder by modified Hummers
110 method.⁴¹ Briefly 24 mL of conc. H_2SO_4 was added into 1 g of graphite powder. Then 0.5 g of
111 NaNO_3 was added into the reaction mixture and cooled to $0 \text{ }^\circ\text{C}$. To the reaction mixture, slowly
112 1.5 g of KMnO_4 was added, and then the temperature was maintained at $20 \text{ }^\circ\text{C}$. The content was
113 heated to $35 \text{ }^\circ\text{C}$ and maintained for 45 min. Then, 46 mL of distilled water was added into the
114 reaction mixture and the temperature of the content was kept at $98 \text{ }^\circ\text{C}$ for 15 min. The reaction
115 was quenched by the addition of 144 mL of distilled water and 1 mL of 30 % of H_2O_2 . The final

116 product was cooled to room temperature and washed with 0.1 M HCl solution for several times
117 and distilled water to remove the metal ions, and then dried.

118 **2.3. Synthesis of AlgCa and GOAlgLa Composite Beads**

119 About 0.5 g of GO was homogeneously dispersed in 100 mL of distilled water. To avoid
120 the agglomeration of GO in water during dispersion, the process was carried out by sonication
121 and followed by mechanical stirring for about 3 h. To the dispersion solution, 2 g of sodium
122 alginate was added and stirred vigorously for 3 h. This homogeneous solution was used to
123 prepare the composite beads by dropping into 0.2 molL^{-1} of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ aqueous solution to get
124 GOAlgLa composite beads. AlgCa composite beads were synthesized by, 2 g of sodium alginate
125 was added into 100 mL of distilled water and stirred vigorously for 3 h. Then the homogeneous
126 alginate solution was dropped into 0.2 molL^{-1} of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ solution to get AlgCa composite
127 beads. Then, the formed AlgCa and GOAlgLa composite beads were kept in the mother solution
128 for about 24 h to take place the complete cross-linking reaction. The prepared AlgCa and
129 GOAlgLa composite beads were separated from the solution, washed with distilled water and
130 dried in hot-air oven at $80 \text{ }^\circ\text{C}$ for 10 h. Finally the dried AlgCa and GOAlgLa composite beads
131 were used for defluoridation studies.

132 **2.4. Adsorption Experiments**

133 Fluoride adsorption experiments were carried out in batch mode in duplicate. About 0.1 g
134 of GOAlgLa composite beads was added to iodine flask containing 50 mL of 20 mg L^{-1} initial
135 fluoride concentration at 303 K. The contents were shaken in thermostat shaker with a constant
136 speed of 200 rpm. To evaluate the effect of contact time, the contents of the iodine flask was
137 taken out at different time intervals viz., 10, 20, 30, 40, 50, 60 and 70 min, the solution was
138 filtered and final fluoride concentration was measured. The impacts of solution pH on the

139 fluoride adsorption processes were carried out by adjusting the pH to 3, 5, 7, 9, and 11,
140 respectively, with 0.1 M HCl/NaOH solution. The initial fluoride concentrations varied from 18,
141 20, 22, and 24 mg L⁻¹ at three various temperatures viz., 303, 313 and 323 K respectively. The
142 amount of fluoride removed by GOAlgLa composite beads was taken as the difference between
143 the initial and equilibrium concentrations of fluoride in the solution and the defluoridation
144 capacity (mgF⁻ kg⁻¹) of GOAlgLa composite beads was obtained by the following equation.

$$145 \text{ Defluoridation capacity (DC)} = \frac{C_i - C_e}{m} V \times 1000 \text{ mgF}^- \text{ kg}^{-1}$$

146 where C_i is the initial fluoride concentration (mg L⁻¹), C_e is the equilibrium fluoride
147 concentration (mg L⁻¹), V is the volume of the solution (L), and m is the mass of the adsorbent
148 (g).

149 2.5. Analytical Methods

150 The fluoride concentration present in the solution was measured using Thermo Orion
151 Benchtop multiparameter kit (Model: VERSA STAR92) using fluoride ion selective electrode
152 having the relative accuracy of ±1 significant digit, detection limit of 0.02 mg L⁻¹ and the
153 reproducibility of ±2 %. The pH measurements were done with the same instrument (Model:
154 VERSA STAR92) using pH electrode (Orion 8157BNUMD). All other water quality parameters
155 were investigated using standard methods.⁴²

156 2.6. Instrumentation Studies

157 The FTIR spectra of the hybrid beads were recorded using a JASCO-460 plus
158 spectrometer operated at 1 cm⁻¹ resolution in the range of 400-4000 cm⁻¹ region using KBr
159 pellets. TEM images were recorded using TEM CM 200 (Philips) model. The surface
160 morphology of the hybrid beads was imagined by scanning electron microscopy (SEM) with
161 Vega3 Tescan model. The change in the surface morphology of the fresh and fluoride sorbed

162 composite beads were obtained by the SEM analysis. The energy dispersive X-ray analyzer
163 (EDAX) of the composite beads was determined using Bruker Nano GMBH model. The pH at
164 zero point of charge (pH_{zpc}) of the composite beads was measured using pH drift method.⁴³

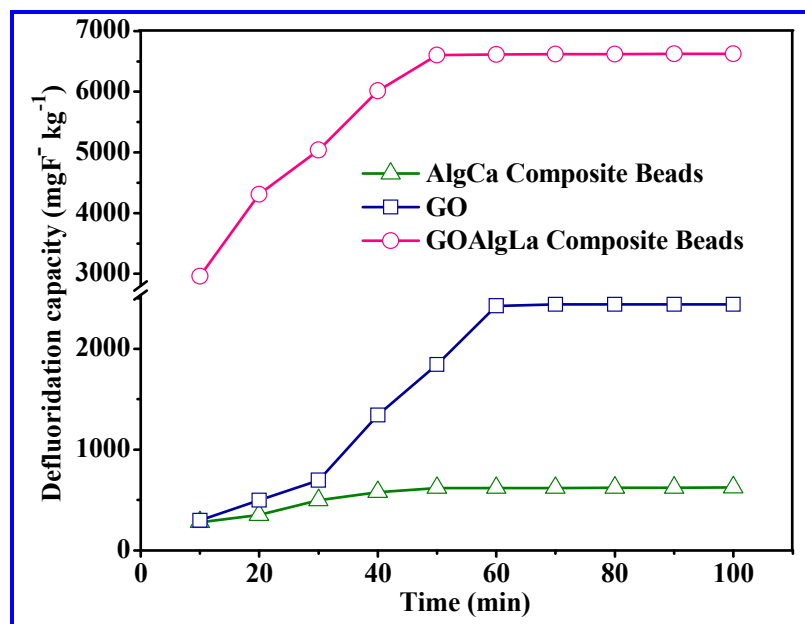
165 2.7. Statistical Tools

166 The computations of the obtained experimental results were carried out using Microcal
167 Origin (Version 8.0) software. The best model and goodness of the fit was find out using the
168 regression correlation coefficient (r), standard deviation (sd) and chi-square analysis (χ^2).

169 3. RESULTS AND DISCUSSION

170 3.1. Effect of Contact Time on the DCs of the Sorbents

171 The sorption performance of GO, AlgCa composite beads and GOAlgLa composite beads for
172 fluoride removal in relation to contact time was carried out by varying the contact time from 10
173 to 100 min for a 50 mL of 20 mg L^{-1} fluoride solution with a dosage of 0.1 g at neutral pH.



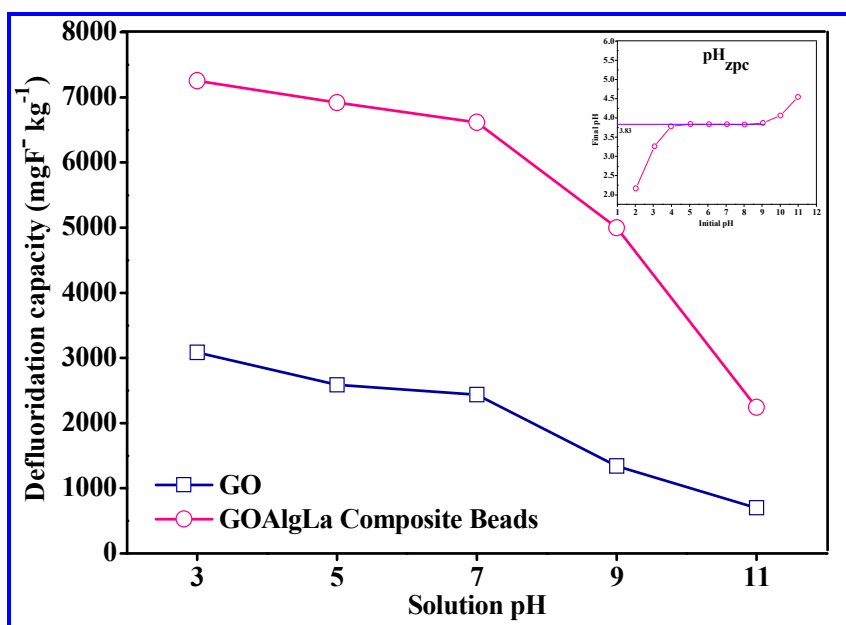
174
175 **Fig. 1.** Effect of Contact Time on the DCs of GO and GOAlgLa Composite Beads.

176 The results are shown in Fig. 1. It was found that, the equilibrium time for the sorption of
177 fluoride onto AlgCa and GOAlgLa composite beads was found to be 50 min, whereas 60 min for

178 GO. The maximum DCs obtained at the equilibrium time of AlgCa, GO and GOAlgLa was
 179 found to be 618, 2438 and 6617 $\text{mgF}^- \text{kg}^{-1}$ respectively. Among the sorbents, GO and GOAlgLa
 180 composite beads possess the higher DC than AlgCa composite beads. Therefore further studies
 181 were limited to GO and GOAlgLa composite beads.

182 3.2. Impact of Solution pH on the Sorption

183 The solution pH is one of the major factors, which alters the net charges of the adsorbent
 184 influencing the adsorption properties. Fig. 2 shows that the impact of solution pH on the fluoride
 185 removal by GO and GOAlgLa composite beads at various initial pH ranges between 3 to 11.



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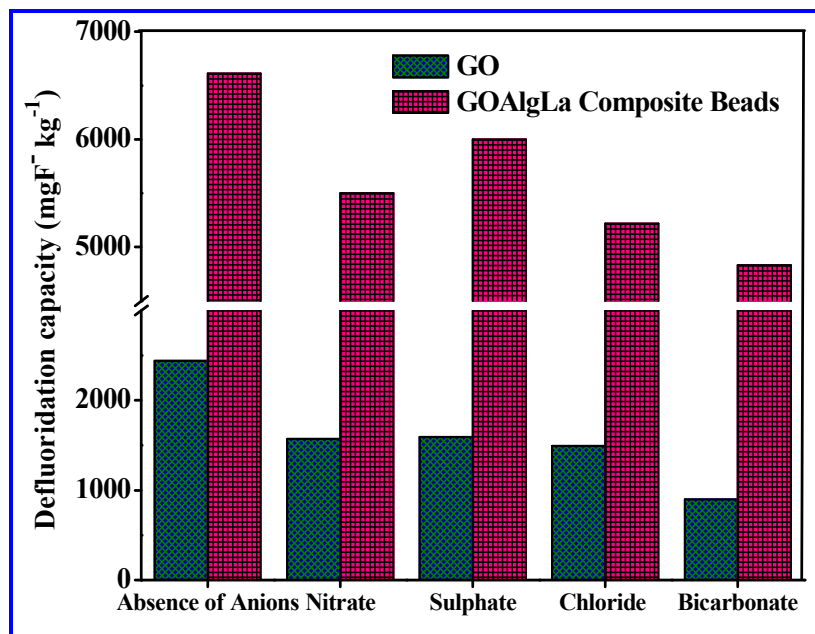
187 **Fig. 2.** Effect of Solution pH on the DCs of GO and GOAlgLa Composite Beads.

188 The maximum DC of GO and GOAlgLa composite beads was found to be 3085 and 7254 mgF^-
 189 kg^{-1} respectively at pH 3 after which the fluoride sorption efficiency of the sorbents decreased
 190 with increasing pH. In general, the adsorbent surface is negatively charged at $\text{pH} > \text{pH}_{\text{zpc}}$, and
 191 positively charged at $\text{pH} < \text{pH}_{\text{zpc}}$. The pH_{zpc} value of GOAlgLa composite beads was found to be
 192 3.83 (inserted in Fig. 2), below which the surface of sorbent possess positively charge favoring
 193 fluoride sorption. When pH increases, the surface of the sorbent turn into less positively charged

194 and the interaction between the fluoride and sorbent becomes less and changes to a repulsive
195 force at $\text{pH} > \text{pH}_{\text{zpc}}$, resulting in the significant decrease of fluoride sorption. The change of the
196 electrostatic force between fluoride and sorbent explains the pH impact on fluoride removal.

197 3.3. Competitive Sorption of Fluoride on the Sorbents

198 The co-existing competitive anions like chloride, nitrate, sulphate, and bicarbonate ions
199 that are usually present in the drinking water might interfere with the fluoride adsorption process.
200 So in order to analyze the effect of these anions on the DCs of GO and GOAlgLa composite
201 beads, studies were carried out by taking 0.1 g of the composite beads which were added to 20
202 mg L^{-1} fluoride solution along with 200 mg L^{-1} competitive anions, the results are presented in
203 Fig. 3. The results reveal that the co-existing anions like chloride, nitrate, and sulphate ions
204 slightly interferes with GO and GOAlgLa composite beads during the fluoride removal, whereas
205 the bicarbonate shows momentous effect on the DC of GO and GOAlgLa hybrid beads.



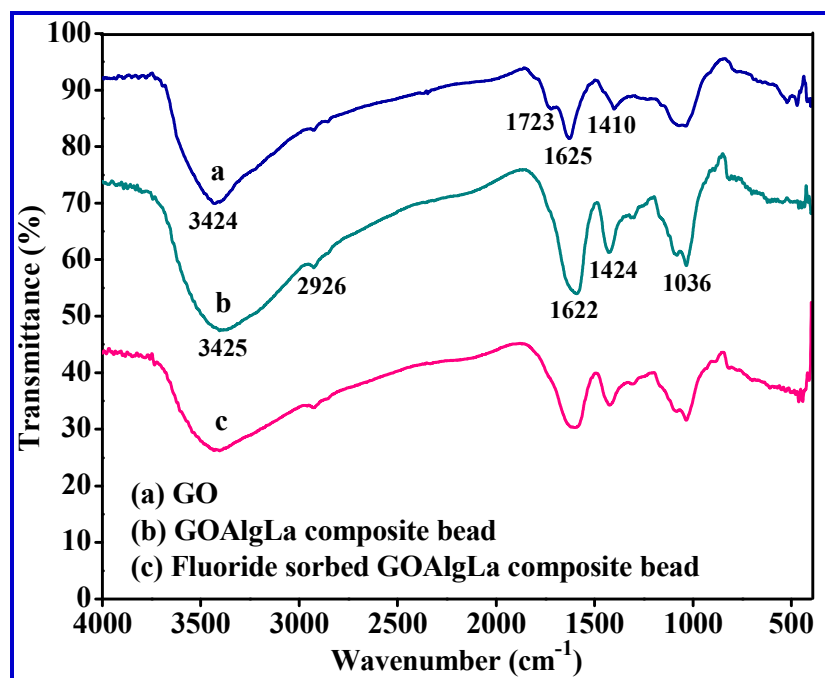
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207 **Fig. 3.** Effect of Competitive Anions on the DCs of GO and GOAlgLa Composite Beads.

208 The decline in the DC of GO and GOAlgLa composite beads in the presence of HCO_3^- ion could
209 be a competition between the HCO_3^- and fluoride ion for the active sites on the adsorbent
210 surfaces, which is decided by the concentration, charge and size of the anions. In addition to this,
211 HCO_3^- ion will increase the solution pH which diminishes the active sites for fluoride sorption.
212 Among the sorbents, GOAlgLa composite beads possess an enhanced DC than GO. Hence, the
213 isotherm and field studies were restricted to GOAlgLa composite beads.

214 3.4. Characterization of GOAlgLa Composite Beads

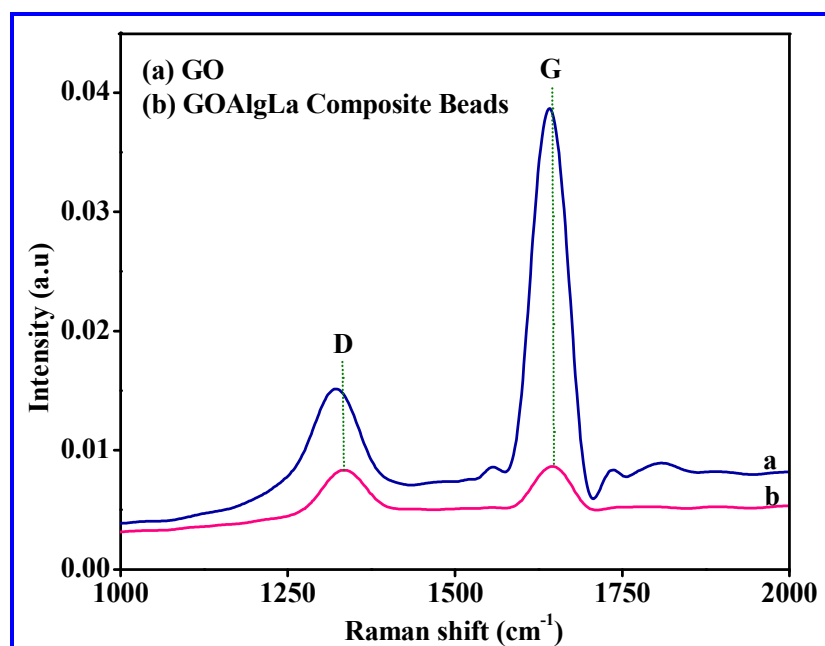
215 FTIR spectra of GO and GOAlgLa composite beads and fluoride sorbed GOAlgLa
216 composite beads are shown in Fig. 4a, b, and c respectively. The FTIR spectra of GO display a
217 peak at 1723 cm^{-1} which is attributed to the C=O stretching of the $-\text{COOH}$ group and the bands
218 presented at $(1410\text{ and }1625)\text{ cm}^{-1}$ owing to stretching vibration of C–O–H of phenolic groups,
219 and (C=C) of aromatic rings respectively.⁴⁴



220
221 **Fig. 4.** FTIR Spectra of (a) GO, (b) GOAlgLa Composite Beads and (c) Fluoride Sorbed
222 GOAlgLa Composite Beads.

223 In GOAlgLa composite beads the bands appeared at 1036, 1424, 1622, 2926, and 3425 cm^{-1} are
224 accredited to the C-O-C stretching, $-\text{CH}_2$ bending, $-\text{COO}-$ asymmetric stretching, $-\text{CH}_2$
225 stretching, and $-\text{OH}$ stretching vibrations respectively.²⁰ The decrease in the intensity of the band
226 at 3409 cm^{-1} in the fluoride sorbed GOAlgLa composite beads was owing to the exchangeable
227 hydroxyl ions present in the composite beads being replaced by the fluoride ion from aqueous
228 solution.

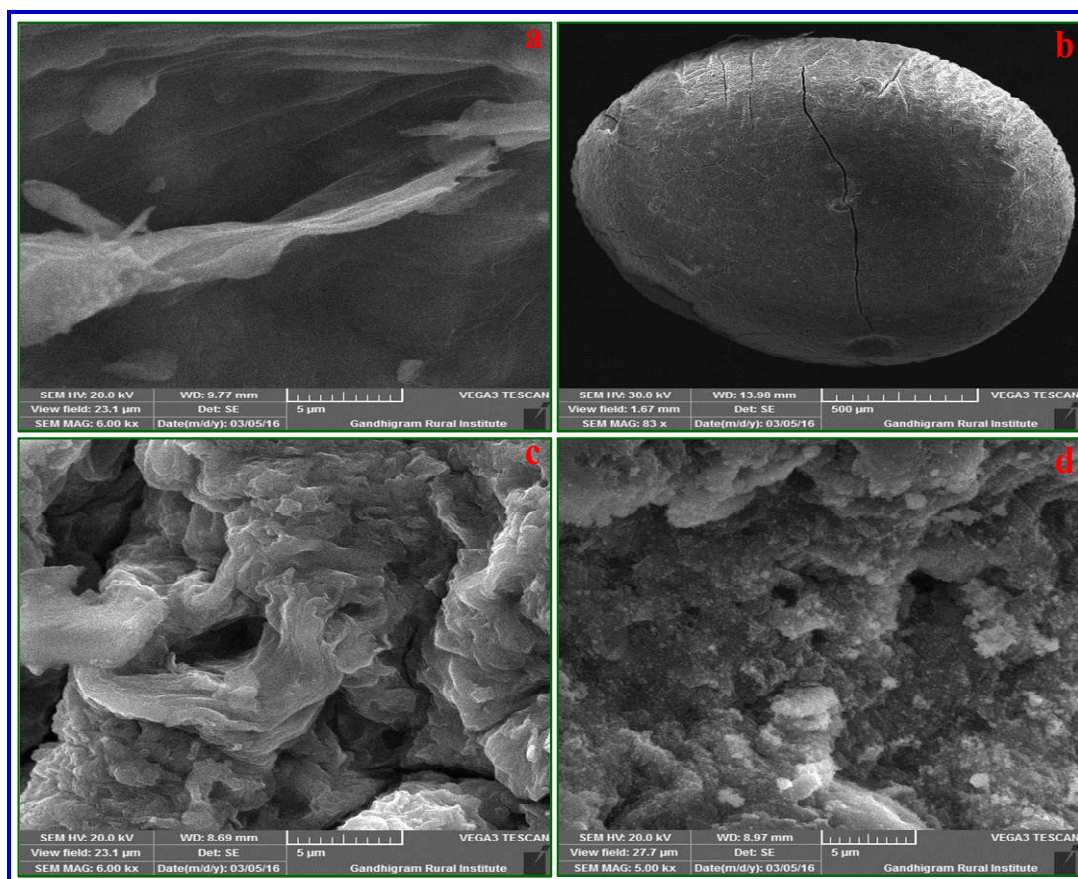
229 Raman spectroscopy is a widely used and definite technique to examine the structural and
230 electronic properties of GO. Fig. 5a and b displays Raman spectrum of GO and GOAlgLa
231 composite beads and the spectra possess two major peaks, namely the D and G band. The strong
232 bands are attributed at ~ 1330 and 1603 cm^{-1} corresponds to D and G band respectively. The D
233 band is the edge-induced disordered related to the presence of sp^3 defects and the G band is
234 associated to the in-plane vibration of sp^2 (C=C) aromatic carbon structure.⁴⁵ Both FTIR and
235 Raman analysis results shows that GO was highly dispersed in the alginate polymeric matrix.



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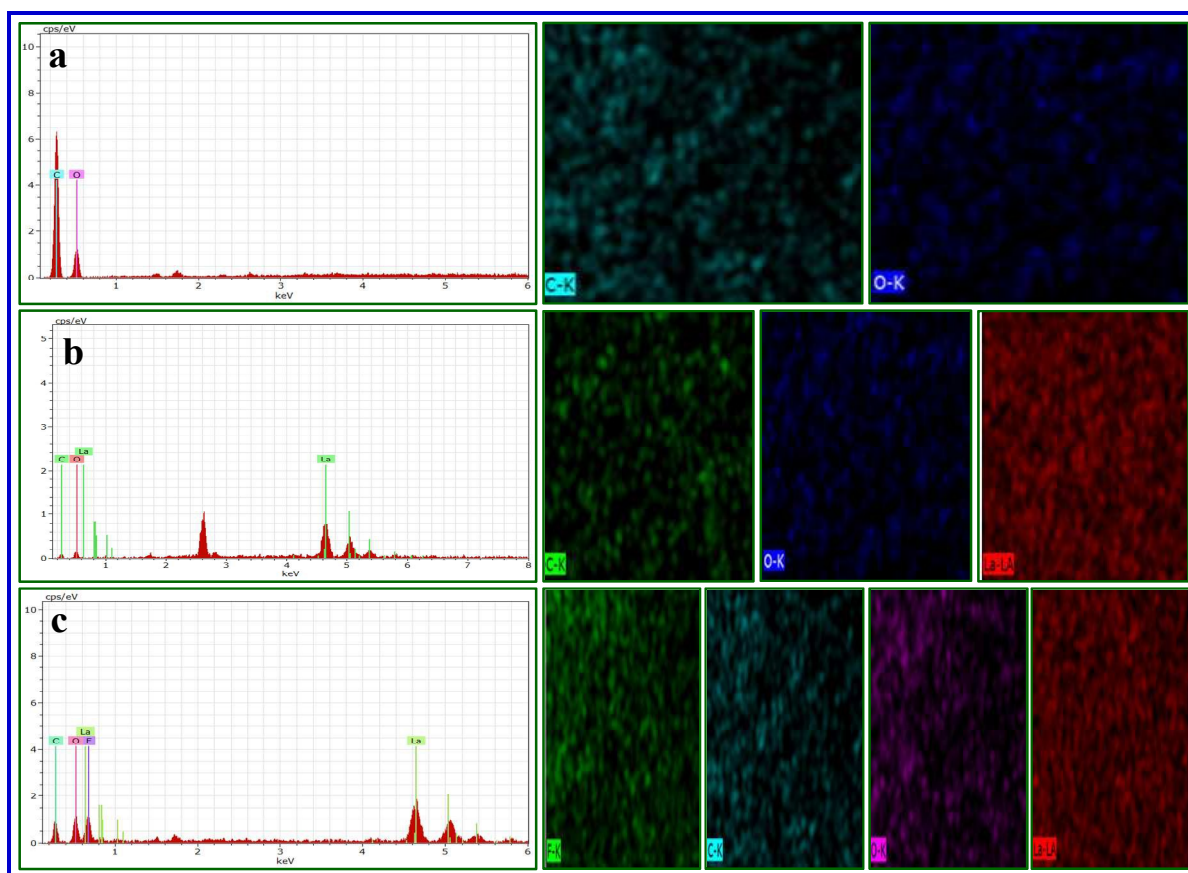
237 **Fig. 5.** Raman Spectra of (a) GO and (b) GOAlgLa Composite Beads.

238 The surface morphology of GO, full image of GOAlgLa composite bead, close view of
 239 GOAlgLa composite bead and fluoride sorbed GOAlgLa composite beads was studied by the
 240 SEM and the results are presented in Fig. 6 a-d respectively. The micrograph images of GO
 241 shows that the loosening of GO nano-sheets and their porous structure due to the opening of
 242 planner carbon networks. In GOAlgLa composite beads, alginate possesses a wide surface and
 243 acted as a bed/support for GO. The SEM image of GOAlgLa composite beads indicates that
 244 distinct porous structures are present in the composite beads and are expected to have more
 245 adsorption sites for the removal of fluoride. After fluoride sorption, the porous structure and
 246 grooves were decreased in GOAlgLa composite beads indicating the fluoride sorption.



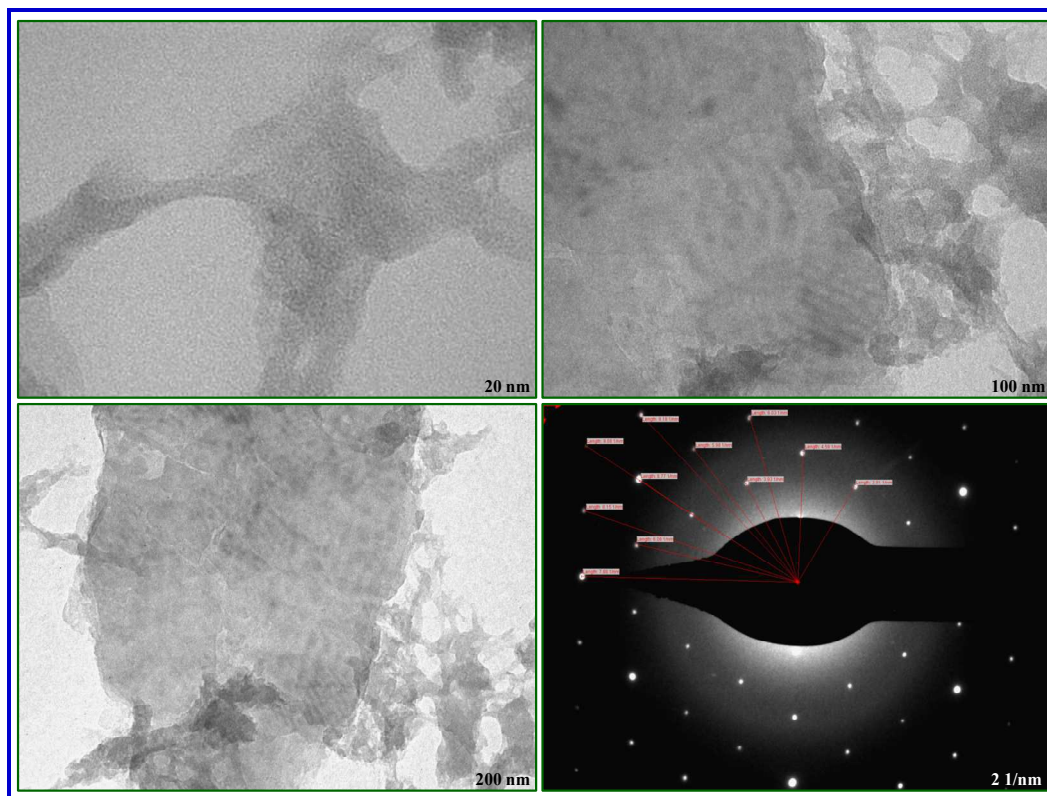
247
 248 **Fig. 6.** SEM Images of (a) GO (b) Overall shape of GOAlgLa Composite Bead. Close-view SEM
 249 images of (c) GOAlgLa Composite Beads and (d) Fluoride Sorbed GOAlgLa Composite Beads.

250 The fluoride sorption to GOAlgLa composite beads was also confirmed by EDAX
251 analysis. GO contains C and O peaks (cf. Fig. 7a), GOAlgLa composite beads possesses C, H,
252 and La peaks (cf. Fig. 7b) and the fluoride sorbed GOAlgLa composite beads possesses C, H, La,
253 and F peaks, which confirms the adsorption of fluoride onto GOAlgLa composite beads (cf. Fig.
254 7c). The mapping image results are also given to confirm the fluoride sorption onto GOAlgLa
255 composite beads. The corresponding colors represent the particular elements present in
256 GOAlgLa composite beads. After fluoride sorption, the presence of fluoride color with the other
257 elements indicates that the fluoride sorption is occurred on GOAlgLa composite beads.



258 **Fig. 7.** EDAX spectra of (a) GO, (b) GOAlgLa Composite Beads and (c) Fluoride Sorbed
259 GOAlgLa Composite Beads.
260

261 The surface morphology of GOAlgLa composite beads was also analyzed by TEM
262 analysis and the results are illustrated in Fig. 8. It indicates that composite beads exhibited
263 transparent and slightly aggregated morphologies with crinkles. In addition, GO was
264 unidirectionally dispersed in the alginate polymeric matrix.



265

266

Fig. 8. TEM Images of GOAlgLa Composite Beads

267 3.5. Sorption Isotherms

268 The sorption isotherm models were used to describe solute-sorbent interaction and
269 optimizing conditions for the maximum sorption. To estimate the fluoride sorption efficiency of
270 GOAlgLa composite beads, three significant isotherms viz., Freundlich,⁴⁶ Langmuir,⁴⁷ and
271 Dubinin-Radushkevich (D-R)⁴⁸ were used. The linear plot of $\log q_e$ vs. $\log C_e$ signifies that the
272 applicability of Freundlich isotherm. The obtained $1/n$, n and k_F values are presented in Table 1.
273 The n values lie between 1 to 10 and $1/n$ values lie between 0 to 1 corresponds to the favorable

274 conditions for fluoride sorption. A linear plot of Langmuir isotherm is acquired for the GOAlgLa
 275 composite beads when C_e/q_e is plotted against C_e which gives b and Q^0 values from intercept and
 276 slope respectively. The calculated values of Q^0 and b are listed in Table 1. The R_L values lie in
 277 the range between 0 and 1 indicates the favorable sorption. The linear plot of $\ln q_e$ vs. ε^2 indicates
 278 the applicability of D-R isotherm.

279 **Table 1. Isotherm Parameters of GOAlgLa Composite Beads**

Isotherms	Parameters	Temperature		
		303 K	313 K	323 K
Freundlich	1/n	0.328±0.020	0.379±0.019	0.437±0.008
	n	3.072±0.005	3.416±0.006	3.498±0.005
	k_F (mg g ⁻¹) (L mg ⁻¹) ^{1/n}	4.897±0.003	5.049±0.010	5.169±0.012
	r	0.991±0.006	0.984±0.015	0.987±0.010
	sd	0.065±0.007	0.071±0.009	0.079±0.004
	χ^2	1.6E-3±0.008	2.0E-3±0.011	2.1E-3±0.007
Langmuir	Q^0 (mg g ⁻¹)	6.701±0.002	6.869±0.008	7.005±0.005
	b (L g ⁻¹)	1.864±0.005	1.919±0.008	2.175±0.003
	R_L	0.167±0.003	0.176±0.001	0.183±0.008
	r	0.998±0.001	0.997±0.002	0.999±0.001
	sd	0.009±0.006	0.017±0.009	0.011±0.014
	χ^2	1.1 E-3±0.002	1.7E-4±0.006	2.58E-4±0.005
Dubinin-Radushkevich (D-R)	X_m (mg g ⁻¹)	5.649±0.022	5.764±0.015	6.194±0.017
	E (kJ mol ⁻¹)	8.698±0.031	9.064±0.120	9.341±0.045
	r	0.994±0.005	0.990±0.002	0.993±0.007
	sd	0.038±0.004	0.029±0.009	0.047±0.006
	χ^2	1.4E-3±0.013	1.8E-3±0.007	1.9E-3±0.014

280
 281 The values of K_{DR} , X_m , and E are shown in Table 1. The E value ranges from 1.0 to 8.0 kJ mol⁻¹
 282 indicates physical sorption and from 9.0 to 16.0 kJ mol⁻¹ for chemical sorption. The obtained E
 283 values are 8.698, 9.064 and 9.341 kJ mol⁻¹ for 303, 313 and 323 K respectively which indicate

284 the defluoridation mechanism of GOAlgLa composite beads is purely chemical in nature. The
 285 higher r values and the lower sd values designate the suitable isotherm.

286 The best isotherm fit was identified using low chi-square (χ^2) values. The calculated chi-
 287 square values are presented in Table 1. The best isotherm fit model follows the order: Langmuir
 288 > D-R > Freundlich for fluoride sorption onto GOAlgLa composite beads.

289 3.6. Thermodynamic Studies

290 The thermodynamic parameters namely, standard free energy change (ΔG°), standard
 291 entropy change (ΔS°) and standard enthalpy (ΔH°) are commonly used to estimate the nature and
 292 feasibility of adsorption and they were calculated by Khan and Singh method⁴⁹. The obtained
 293 results are shown in Table 2. The ΔG° values are negative and increases with increasing
 294 adsorption temperature, which signifies the feasibility and spontaneity of fluoride sorption on
 295 GOAlgLa composite beads. The positive values of ΔH° indicate the endothermic nature of
 296 fluoride sorption. The positive value of ΔS° reveals the increase in the number of species and
 297 randomness at the solid-liquid interface.

298 **Table 2. Thermodynamic Parameters of GOAlgLa Composite Beads**

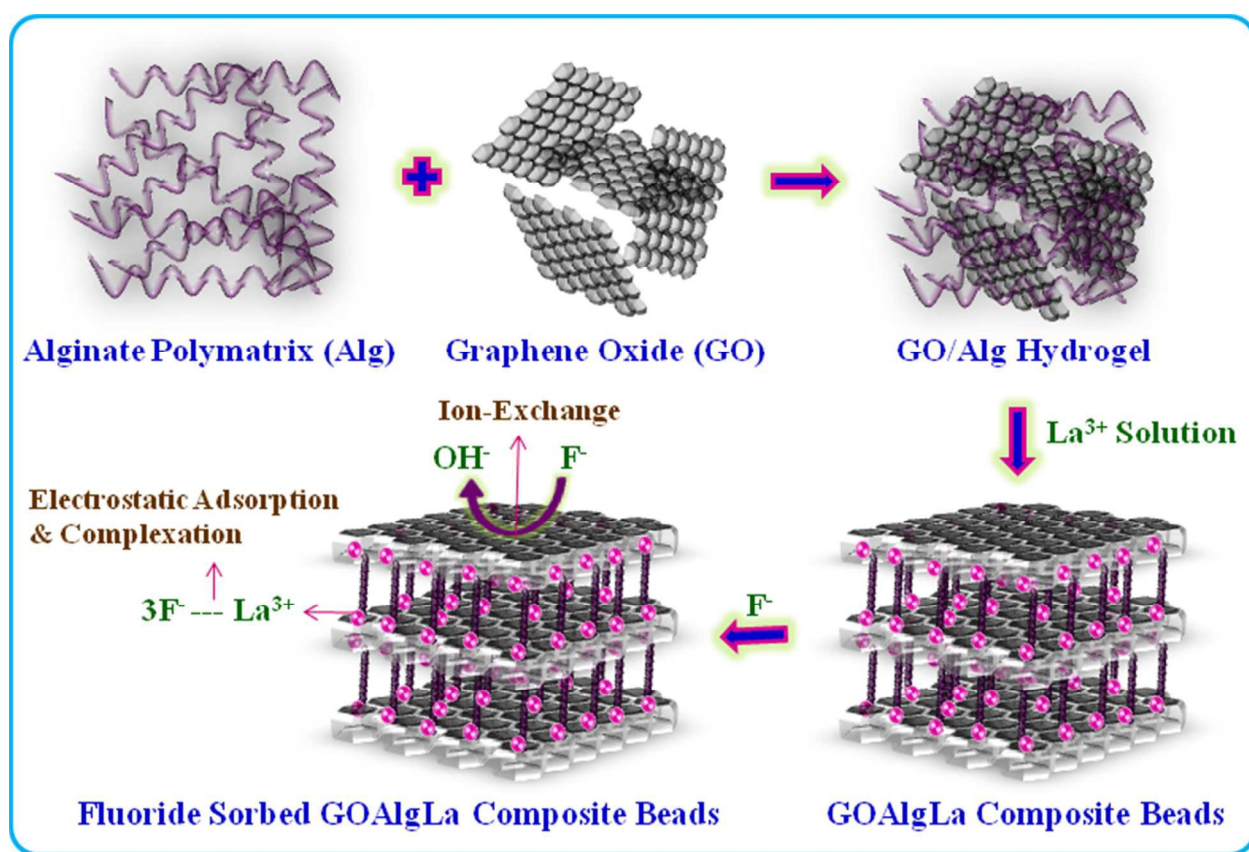
Thermodynamic Parameters	Temperature	
ΔG° (kJ mol ⁻¹)	303 K	-4.28
	313 K	-3.84
	323 K	-3.16
ΔH° (kJ mol ⁻¹)		16.67
ΔS° (J K ⁻¹ mol ⁻¹)		57.00

299

300

301 3.7. Mechanism of Fluoride Uptake on GOAlgLa Composite Beads

302 The graphical representation of fluoride removal by GOAlgLa hybrid beads is shown in
 303 Fig. 9. It shows that the fluoride removal by GOAlgLa composite beads was governed by both
 304 ion-exchange and electrostatic adsorption mechanism. The surface of GO is positively charged
 305 with hydroxide as negative counter anions. Therefore the higher electronegative fluoride ion
 306 easily replaces the hydroxyl anion by ion-exchange mechanism. Secondly, the positively charged
 307 La^{3+} ions present in GOAlgLa composite beads attracts the negatively charged fluoride ions by
 308 means of electrostatic adsorption and complexation mechanism.



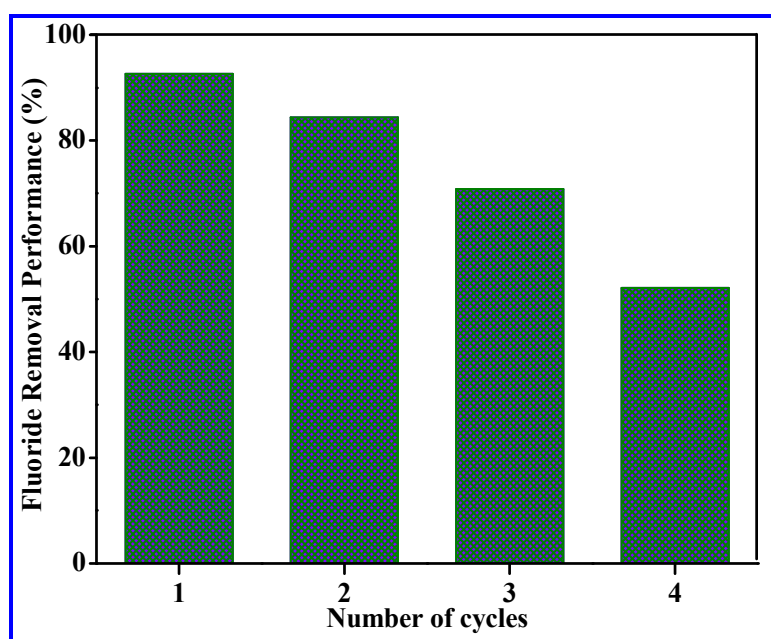
309

310 **Fig. 9.** Feasible Fluoride Removal Mechanism of GOAlgLa Composite Beads.

311 3.8. Desorption and Reusability Studies of GOAlgLa Composite Beads

312 In practical application, the regeneration and recycling of the adsorbents is indispensable.
 313 After fluoride sorption studies, GOAlgLa composite beads was separated by simple filtration,

314 washed with double distilled water, dried and reused for further adsorption-desorption cycle.
315 During adsorption studies, 0.1 g of GOAlgLa composite beads was added to 50 mL of fluoride
316 solution with initial concentration of 20 mg L^{-1} for 50 min at neutral pH. After that, the fluoride
317 sorbed GOAlgLa composite beads (13.30 mg L^{-1}) were separated by simple filtration, washed
318 with double distilled water and left for drying. The dried GOAlgLa composite beads was added
319 to the dilute NaOH solution (50 mL) with various concentrations ranging from 0.02 to 0.1 M.
320 Desorption of fluoride from GOAlgLa composite beads was improved from 0.02 to 0.1 M. The
321 maximum desorption efficiency of 92.6 % (12.32 mg L^{-1}) of the composite beads was achieved
322 with 0.1 M of NaOH solution as a regenerant. From Fig. 10, it is clearly shows that the fluoride
323 sorption efficiency of GOAlgLa composite beads was decreased and was found to be 92.6 (12.32
324 mg L^{-1}), 84.4 (11.23 mg L^{-1}), 70.8 (9.42 mg L^{-1}), and 52.1 (6.93 mg L^{-1}) % in fresh to four cycles
325 respectively. In each cycle the fluoride removal efficiency was decreased gradually and after four
326 cycles the fluoride removal reached minimum. It suggests that GOAlgLa composite beads could
327 be regenerated and can be effectively used upto four cycles.



328

329

Fig. 10. Reusability studies of GOAlgLa Composite Beads.

330 3.9. Removal of Fluoride from Field Water Sample

331 The application of GOAlgLa composite beads at field conditions was tested by collecting
332 bore-well water sample from a nearby fluoride widespread area. About 50 mL of fluoride
333 contaminated water sample was shaken with 0.1 g of GOAlgLa composite beads for 60 min at
334 room temperature and the results are shown in Table 3. The observed concentration of fluoride in
335 field water sample was 3.28 mg L^{-1} which is higher than the value recommended by WHO i.e., >
336 1.5 mg L^{-1} . After the treatment the fluoride concentration has been greatly reduced to below the
337 tolerance limit showing the efficiency of GOAlgLa composite beads. (cf. Table 3). The result
338 also reveals the selectivity of GOAlgLa composite beads towards fluoride, as the field water
339 sample also contain higher concentration of other anions other than fluoride. It is interesting to
340 note that, the level of other water quality parameters has also been reduced to some extent.
341 Hence GOAlgLa composite beads can be efficiently employed for defluoridation of water.

342 **Table 3. Field Trial Results of GOAlgLa Composite Beads**

Water Quality Parameters	Before Treatment	After Treatment
F^{-} (mg L^{-1})	3.28	0.72
pH	7.68	7.75
Cl^{-} (mg L^{-1})	617	486
Total hardness (mg L^{-1})	376	351
Total dissolved solids (mg L^{-1})	709	658

343

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345

346 **3.10. Performance Comparison of GOAlgLa Composite Beads with Other Adsorbents**

347 A comparative review was carried out for GOAlgLa composite beads with other previous
 348 reported adsorbents. Table 4 shows that the fluoride adsorption capacities GOAlgLa composite
 349 beads have appreciable adsorption capacities with the reported adsorbents.

350 **Table 4. Fluoride Adsorption Capacity of Different Adsorbent Materials**

S.No.	Name of the Adsorbent	Adsorption Capacity (mg g ⁻¹)	Reference
1	GOAlgLa composite beads	6.62	Present study
2	Bauxite clay	5.16	50
3	Zn/Al and Mg/Al intercalated sodium alginate	5.10	51
4	Al-Zr in cellulose matrix	5.76	52
5	Corn stover biochar (CSBC)	6.42	53
6	Magnetic corn stover biochar (MCSBC)	3.61	53
7	La(III) loaded hematite	0.36	54
8	La loaded zeolite	0.36	54
9	Fe-Al-impregnated granular ceramic	3.56	55
10	Calcium chloride modified natural zeolite	1.77	56
11	Magnesia-loaded fly ash cenospheres	6.00	57
12	La(III) incorporated carboxylated chitosan beads	4.71	58
13	Waste carbon slurry	4.31	59
14	La(III) cross-linked nano-hydroxyapatite alginate composite beads	3.72	21
15	Fe ₃ O ₄ coated nano-hydroxyapatite gelatin composite	5.01	10
16	Chitosan supported lanthanum/zirconium mixed oxide composite	4.97	60
17	Activated carbon (<i>Acacia farnesiana</i>)	2.62	61
18	Siderite (modified)	5.46	62
19	Stilbite zeolite modified with Fe(III)	2.31	63
20	Cellulose@HAP nanocomposites	2.76	64
21	Hydrous bismuth oxides	1.93	65

22	HFO doped alginate beads	8.90	66
23	Zirconium-iron oxide	9.80	67
24	Zirconium phosphate	4.27	68
25	Aluminum (hydr)oxide coated pumice	7.87	69
26	Alginate impregnated alumina	17.00	34
27	KMnO ₄ modified carbon	15.90	70
28	Granular ceramic	12.12	71
29	Chemical treated laterite	37.90	72
30	Magnetic chitosan	22.49	73

351

352 **4. CONCLUSIONS**

353 The hybrid biopolymeric composite beads was synthesized by incorporating GO in Alg
354 polymeric matrix and followed by cross-linking with La(III) metal ion. The developed GOAlgLa
355 composite beads showed a potential efficiency for the removal of fluoride from aqueous solution.
356 The DC of GOAlgLa composite beads decreased drastically when the solution pH was raised
357 from 3 to 11. The presence of competitive anions like chloride, nitrate, and sulphate ions are not
358 considerably decrease the DC of GOAlgLa composite beads. However, bicarbonate ion retarded
359 the DC of GOAlgLa composite beads. The sorption isotherm process was fitted well with
360 Langmuir isotherm than D-R, and Freundlich models. GOAlgLa composite beads posses higher
361 DC than GO because its removes fluoride by ion-exchange, electrostatic adsorption and
362 complexation. The thermodynamic parameters values indicate the spontaneous and endothermic
363 nature of fluoride removal. The regeneration and reusability studies indicate that the performance
364 of GOAlgLa composite beads for continuous applications. The results of field application of
365 GOAlgLa composite beads illustrates that the biopolymeric composite beads can be efficiently
366 utilized for fluoride sorption and it will make a platform to develop the defluoridation
367 technology.

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GRAPHICAL ABSTRACT

