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Adsorption Potential of Goethite Rich Iron Ore from Daitari Mines towards Removal of Aqueous Fluoride

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ABSTRACT

The present study demonstrated the adsorption potential of goethite rich iron ore (GRI) of Daitari, Orissa, India under various pH, adsorbent dose, initial fluoride concentration and presence of major co-existing anions. Adsorption of fluoride on GRI was relatively fast in first 2 h followed by slow adsorption leading to equilibrium within 4-5 h. Maximum adsorption was achieved in the pH range of 4.5-5.5. The time course adsorption data was well fitted to both first-order and pseudo second-order rate expression while the experimental equilibrium sorption data were better to Freundlich isotherm indicating that the GRI surface was heterogeneous. The presence of co-existing anions also affected fluoride adsorption according to their affinity on the GRI surface in the following order: HCO_3^- > SO_4^{2-} > Cl^-> NO_3^-. Alkaline pH promotes the fluoride desorption, and more than 65 % of adsorbed fluoride was released to solution at pH ~ 10.

1. Introduction

Fluoride is another essential micronutrient with its mixed blessings to many animals including human where, it has both harmful effects if assimilated in excess and equally severe consequences if nutritionally deficient [1-3]. The optimum fluoride level in drinking water for general good health, recommended by WHO and US public water system, is in between 0.5 to 1.5 mg/L [4, 5]. Indian standard for drinking water, also recommended an acceptable fluoride concentration of 1.0 mg/L and an allowable limit of 1.5 mg/L in potable water [6]. Fluoride in groundwater is mostly of geogenic origin arising from breakdown of rocks (e.g. Fluorspar) containing the fluoride ions. In addition, anthropogenic sources such as infiltration of chemical fertilizers in agricultural areas and liquid wastes from industrial entities also contribute to fluoride ions in groundwater.

The widely used current methods for defluoridation of water are broadly divided into two categories: precipitation and adsorption. Precipitation of fluoride with calcium and aluminium salts [7] has been used to remove fluoride from industrial wastewater. However, this technique is not very much suitable for drinking water purpose due to partial solubility of CaF_2 which lead to fluoride concentration in water more than 2 mg/L and also due to increase of pH of treated water which require further treatment for lowering the pH value to the desired level [8,9]. Among other methods like reverse osmosis, electrodialysis, donnan dialysis, ion exchange etc., the adsorption process is most widely used and offers satisfactory results. It seems to be a more attractive method for the removal of fluoride in terms of cost, simplicity of design and operation [10-13]. A wide variety of synthetic materials and naturally occurring minerals or wastes such as activated alumina/modified alumina, amorphous alumina, activated carbon/charcoal, mixed oxides, calcite, clay, zeolite, fly ash, bleaching earth, red mud, iron bearing minerals etc. [8, 14-22] have been used by several researcher and their findings have been reflected in the recent reviews [10-13].

Iron ores from Daitari, Orissa iron mines usually contain substantial amount of structural water, primarily in the form of goethite, which makes the ore unsuitable for direct utilization in the blast furnaces. Hence exploration of adsorption and catalytic properties can open up avenues for alternate uses of such ores or even further lower grade ores that contains goethite as a major mineral. Keeping the above in view and in sequel to our previous study on physicochemical characterizations and sorption behaviours of a goethite rich iron ore towards different oxyanions [23], the present study investigates its adsorption potential towards aqueous fluoride under varying experimental parameters. The effects of heat treatment on goethite: hematite ratio and sorption capacities of resulted products have also been studied.

2. Experimental Methods

2.1 Materials

Goethite rich iron ore (GRI) was collected from open cast mines of Daitari, Orissa. Processing and characterization of GRI samples (as such and their calcined products) by various physicochemical techniques (XRF, XRD, SEM-EDX, TG-DTA, FT-IR, UV-Vis-DRS and optical microscopy) were same as described in earlier studies [23]. The calcined GRI-0 samples at 100, 200, 300, 400 and 500 °C for 3 h were named as GRI-100, GRI-200, GRI-300, GRI-400 and GRI-500, respectively and were used for adsorption studies. All other chemical used were of analytical grade.

2.2 Sorption and Desorption Experiments

The stock fluoride (250 mgF/L) solution, used for adsorption of fluoride by different samples, was prepared by dissolving required amount of NaF with distilled water in a polypropylene made volumetric flask.

Sorption of fluoride on different samples was carried out by equilibrium method of batch type. Experimental runs were carried out in 100 mL PVC bottle by dispersing certain amount of adsorbent in 50 mL of solution with varying fluoride concentrations. The initial pH of the solution was adjusted by adding dilute NaOH or HCl. The final volume was invariably kept at 50 mL. All the adsorption experiments were carried out at (30±0.5 °C) using a water bath shaker (S.D. Instruments & Equipments). After continuous shaking at constant speed (100 strokes/min) for a predetermined time interval, the solid was separated by centrifuge (REMI, R-24) and the remaining fluoride was estimated spectrophotometrically [5].

The amount of fluoride adsorbed was determined from the ratio of fluoride in the solution and particulate phases using the following equation,

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$$q_e = [(C_t - C_e)V]/m \quad (1)$$

where q_e, C_i, C_e, V and m represent the amount of F adsorbed on the solid (mgF/g), the initial concentration (mg/L), the final concentration (mg/L), volume of the solution (L) and amount of adsorbent (g), respectively.

The reusability of adsorbent mainly depends on the ease with which the adsorbate gets desorbed from loaded adsorbent. For this, a certain amount of fluoride from aqueous solution was initially allowed to adsorb on certain amount of adsorbent at optimum pH. After adsorption, the solid adsorbent was separated and the amount of fluoride adsorbed in the solid was determined by analysing the remaining fluoride in the supernatant. The separated solid in the centrifuge tube was dispersed in 50 mL of deionised water and the pH was adjusted to desired value by addition of NaOH. The whole content was then stirred for a pre-determined period. The solid was then separated again by centrifugation and fluoride in the supernatant was determined by methods described below. The final pH of the solutions was also measured. The fluoride contents in the solution before and after adsorption experiments were estimated.

3. Results and Discussion

3.1 Characteristics of GRI and Effect of Heat Treatment on Sorption of Fluoride

The chemical analyses showed that Fe as the major constituent (63.12 wt.%) of GRI-0 along with Al_2O_3 (1.55), SiO_2 (2.57), S (0.012), P (0.043), Mn (0.217), Na_2O (0.09), K_2O (0.052), TiO_2 (0.09 wt.%) as the minor constituents. PXRD coupled with thermal and optical micrograph analyses showed the presence of significant amount of goethite in GRI-0 which progressively converted to hematite due to loss of structural water on heating and nearly complete conversion was observed at ~ 400 °C [23]. The surface area of GRI-0 is relatively low (~ 5.5 m^2/g) which increases to 49.4 m^2/g on heating at 300 °C and then decreases on further heating.

It has been reported earlier [14, 24] that thermal pre-treatment of hydrous metal oxides strongly influence the adsorption of toxic anions. As such the adsorption fluoride was carried out using raw and calcined GRIs to find the most effective GRI for further variation of parameters. The results obtained are presented in Fig.1. As seen, the heating has a positive effect on fluoride adsorption efficiency and reaches a maximum value with sample calcined at 300 °C, a temperature at which dehydoxylation is almost terminated. The fluoride adsorption capacity of GRI-300 is almost increased by ~1.5 fold from that of GRI-0. The major factor governing the heat activation of GRI is dehydration which causes an increase in surface area and porosity [23] in addition to maintaining the appropriate hematite/goethite ratio for higher adsorption. Heating of GRI-0 at temperature ≥ 400 °C decreases the overall uptake of fluoride due to lowering of surface area and complete conversion of GRI to hematite (Fig. 1, inset). As such all further optimization of fluoride adsorption was carried out using GRI-300.

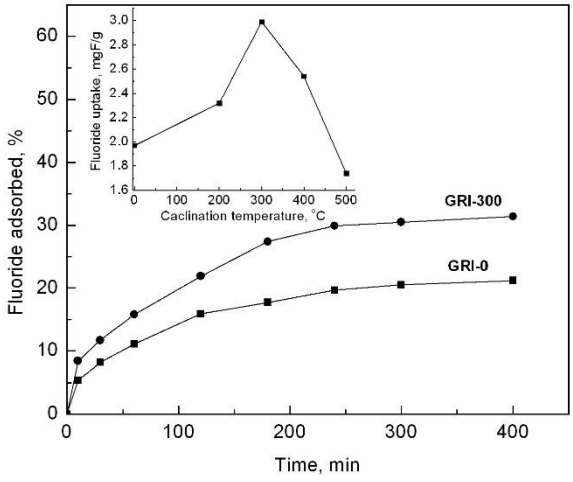

Fig. 1 Effect of contact time on the adsorption of fluoride (10 mg/L) by GRI-0 and GRI-300 at pH ~ 5.0 and 30°C and effect of calcination temperature on overall fluoride uptake (inset)

3.2 Effect of Contact Time and Sorption Kinetics

The time course adsorption of fluoride on GRI-0 and GRI-300 under identical conditions is given in Fig. 1. It is observed that there is an increase of adsorption with time and more than 65 % adsorption takes place in first 2 h followed slow adsorption leading to equilibrium at ~ 4-5 h. Hence all further experiments were carried out keeping the adsorption equilibrium time fixed at 4 h.

The adsorption data are fitted to commonly used Lagergren pseudo-first order (Eq. 2) and pseudo-second-order rate expression (Eq. 3).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where q_e and q_t are the amounts of fluoride (mg/g) on GRI at equilibrium and at time t , respectively, and k_1 (min^{-1}) is the first-order rate constant.

$$t/q_t = (1/k_2) - 1/q_e^2 - + t/q_e \quad (3)$$

where the boundary conditions of t = 0 to t = t and q_t = 0 to $q_t = q_t$ is applied. It is found that the second order equation is slightly better fitted (r^2 = 0.99) than first-order rate equation (r^2 = 0.983) yielding k_1 and k_2 values 1.16×10^{-2} min^{-1} and 7.8×10^{-1} mg g^{-1} min^{-1}, respectively for a fluoride concentration of 10 mgF/L. The first order rate constant compares well with those reported for adsorption fluoride by laterites (1.34×10^{-3} min^{-1}) [17] and iron bearing mineral/wastes {$(3.9\text{-}9.2)\times10^{-3}$ min^{-1}} [18] and granular ferric hydroxide (1.34×10^{-3} min^{-1}) [20]. However, this value is relatively lower than those reported for fluoride adsorption by granular ferric hydroxide (0.346 min^{-1} [22], nano scale oxide-hydroxide (0.97 min^{-1}) [25].

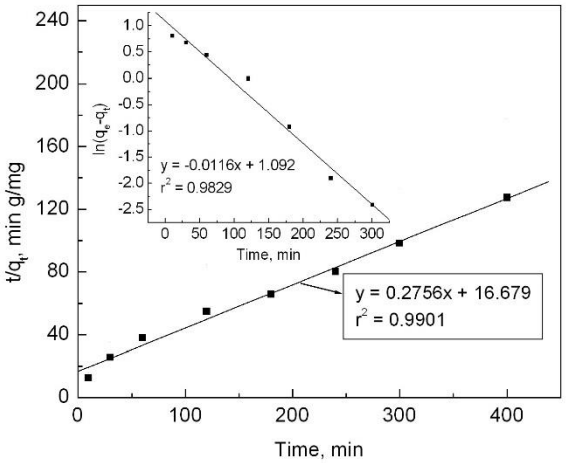

Fig. 2 Lagergen first-order and Pseudo second order fitting of fluoride adsorption on GRI-300 (data corresponds to Fig. 1).

3.3 Effect of pH

As seen in the previous section the pH of the medium greatly affects the adsorption of oxyanions primarily due to variations in charge of adsorbate species and adsorbent surface. The adsorption pattern of fluoride on GRI-300 in the pH range 3 to 10 is presented in Fig. 3. It may be noted that the equilibrium pHs of the solution after adsorption are found 0.2-0.5 units higher than the initially adjusted pH at lower pH range (< 7.0), while it is slightly decreased than the initial pH at above 7.0. This increase of pH is a consequence of two-step ligand exchange mechanism (as delineated below) operated during adsorption of fluoride. Similar observation has also been noted previously by several workers [14, 24]. It is also found that irrespective of initial fluoride concentration the uptake of fluoride is increased with increase of pH, reached maximum at pH ~ 4.5 to 5.5 and then decreased on further increase of pH. This is consistent with the results reported by several workers for adsorption of fluoride [14, 18, 19, 24]. Thus pH range 4.5 to 5.5 is most suitable for fluoride adsorption by this material.

Considering the pHs profile and nature of oxides/oxyhydroxides present in GRI-300, the adsorption of fluoride may be best represented by following two-steps protonation/Ligand exchange mechanism.

$$\equiv SOH_{(s)} + H^+_{(aq)} \rightleftarrows \equiv SOH_{2\,(s)} \quad (4)$$

$$\equiv SOH_{2(s)} + F^-_{(aq)} \rightleftarrows \equiv SF_{(s)} + H_2O \quad (5)$$

which gives the net reaction

$$\equiv SOH_{(s)} + H^+ + F^-_{(aq)} \rightleftarrows \equiv SF_{(s)} + H_2O \quad (6)$$

where, ≡ S represents the surface of adsorbent.

This two-step mechanism is favourable at pH < 6. However, at pH > 6, fluoride ion is predominantly adsorbed by following mechanism:

$$\equiv SOH_{(s)} + F^-_{(aq)} \rightleftarrows \equiv SF_{(s)} + OH^- \quad (7)$$

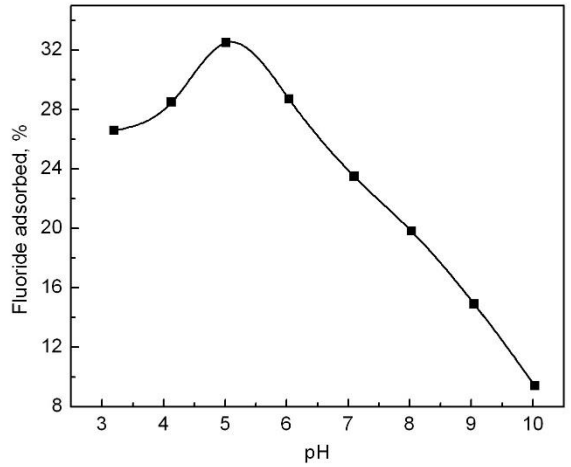

Fig. 3 Effect of solution pH on fluoride adsorption by GRI-300. Initial fluoride, 10 mg/L; adsorbent dose, 1.0 g/L.

The progressive decrease of fluoride uptake at pH > 6 is mainly due to two factors: the electrostatic repulsion of fluoride ion to the negatively charged surface of the GRI-300 (pH_{zpc}= 7.94) and the competition for active sites by excessive amount of hydroxyl ions. Similar findings have also been reported earlier [8, 14, 18, 19, 24]. It may be noted that at pH ≤ pH_{zpc}, the surface charge of GRI-300 is positive while at pH ≥ pH_{zpc}, the surface charge is negative due amphoteric dissociation of iron oxyhydroxide.

3.4 Effect of Adsorbent Dose

The effect of adsorbent (GRI-300) dose on fluoride removal at pH ~ 5.0 and fixed initial fluoride concentration (10 mg/L) is shown in Fig. 4. It is seen that fluoride removal increases with the increase of adsorbent doses while loading capacity (amount of fluoride loaded per unit weight of adsorbent) gradually decreases for the same. This increase in loading is due to availability of greater amount of active sites for fluoride removal. It can also be seen that the fluoride uptake is markedly increased up to adsorbent dose of 2.0 g/L and thereafter no significant increase is observed. This may be presumably due to non-availability of enough fluoride ions for adsorption at the GRI-300 surface. Similar behaviour has also been reported previously for adsorption of fluoride by other adsorbents [14, 18, 19, 24]. The maximum loading capacity is found to be 5.46 mg/g with adsorbent dose of 0.5 g/L.

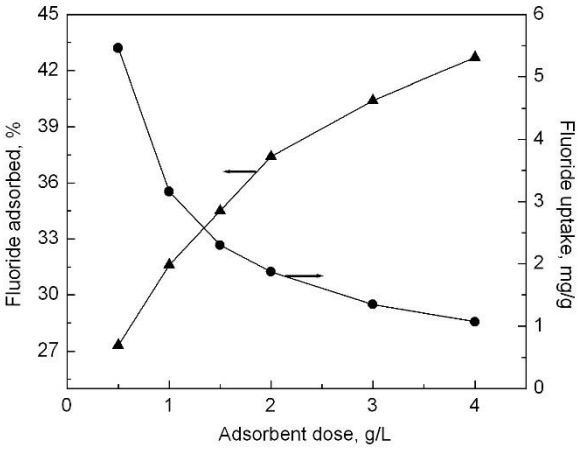

Fig. 4 Effect of adsorbent (GRI-300) dose on fluoride adsorption. Initial fluoride, 10 mg/L; pH ~ 5.0

3.5 Effect of Initial Adsorbate Concentration and Adsorption Isotherms

The effect of initial fluoride concentration on its adsorption over GRI-300 shows that the percentage of adsorption decreases from 37.5 to 20.4 % with increase of fluoride concentration from 5 to 50 mg/L and as expected, there is an increase in the uptake from 1.9 to 10.2 mgF/g. The higher uptake with increasing adsorbates ion concentration are obviously due to the availability of sufficient adsorbate ions for adsorption to occur on the fixed number of adsorption sites available.

The sorption data are fitted to Langmuir and Freundlich isotherms. These models are the simplest and most commonly used isotherms to represent the adsorption of component from liquid phase onto a solid phase. The Langmuir model assumes monolayer adsorption while the Freundlich model is empirical in nature which assumes the adsorption on heterogeneous surface. The equilibrium adsorption data in the range of initial fluoride 5 – 50 mg/L are fitted to linearly transformed Langmuir and Freundlich equations. The Langmuir equation may be expressed as:

$$C_e/(x/m) = 1 / (bX_m) + C_e/X_m \quad (8)$$

where C_e is the equilibrium adsorbate concentration in solution, X_m denotes the amount adsorbed to form monolayer (adsorption capacity), (x/m) is the amount adsorbed per unit mass of adsorbent, and b is the binding energy constant. The Freundlich equation may be expressed as:

$$\log(x/m) = 1/n (\log C_e) + \log K \quad (9)$$

where K and 1/n are constants and considered to be relative indicators of adsorption capacity and adsorption intensity, respectively.

The fittings of adsorption data to Langmuir and Freundlich equations along with derived parameters are presented in Fig. 5. It is evident that Freundlich model is slightly better fitted to the experimental data (r^2 =0.996) than Langmuir model (r^2 =0.975). The derived adsorption parameters along with those reported are presented in Table 1. It may be noted that the derived monolayer adsorption capacity (X_m = 17.9 mgF/g) is comparable with those reported for several iron bearing minerals/waste [18] but higher than laterites [17] and granular ferric hydroxide [22]. However the value is lower than waste iron oxide generated from fluoridised-bed Fenton reaction [19]. This may be partly due to use of relatively high initial concentration of fluoride and higher surface area of the waste oxide.

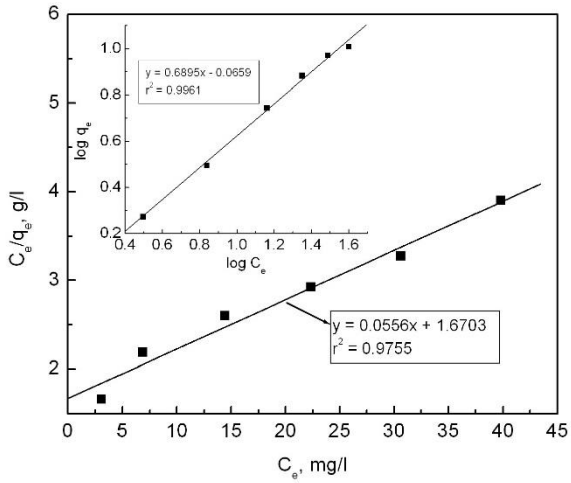

Fig. 5 Fitting of equilibrium adsorption data to Langmuir and Freundlich model.

Table 1 Adsorption parameters derived from Langmuir isotherm along with experimentally obtained maximum fluoride uptake of iron based materials/minerals

Sample description	Surface area, m^2/g	Initial [F^-], mg/L	pH	Langmuir parameters		Ref.
				X_m, (mgF/g)	B (l/g)	
Ni-laterites (Low Fe, 28.6 wt. %)	68	10-50	~ 5.0	12.30	0.02	18
Ni-laterites (High Fe, 46.3 wt. %)	74	10-50	~ 5.0	15.02	0.04	18
Overburden Chromite mines (Low Fe, 28.6 wt. %)	44	10-50	~ 5.0	15.17	0.04	18
Laterites	-	10-50	7.5	0.846	0.1358	17
Waste iron oxide	124.7	114	4.0	27.0	-	19
Granular ferric hydroxide	250-300	1-100	6 - 7	5.97	0.00135	22
GRI-300	49.4	10-50	5.0	17.9	0.033	This study

3.6 Effect of Co-Existing Anions

Natural water may contain many anions that compete with fluoride for adsorption. In this study, effects of HCO_3^-, SO_4^{2-}, NO_3^- and Cl^- were examined at pH ~ 5. The initial concentration of fluoride was kept constant at 10 mgF/L in all experiments, whereas concentrations of other anions were varied from 50-100 mg/L. Fig. 6 shows that the fluoride adsorption is decreased from 32 % to 19 % when the SO_4^{2-} concentration increased from 0 to 100 mg/L. On the other hand, Cl^- has relatively less impact on

fluoride adsorption. Previous studies also revealed that Cl^- formed outer-sphere surface complexes, while SO_4^{2-} formed both outer-sphere and inner-sphere surface complexes [26]. Therefore, the expected impact of Cl^- on fluoride adsorption is less significant than that of SO_4^{2-}. The fluoride adsorption is also decreased substantially when bicarbonate is present in the system. Bicarbonate is a pH buffering agent and its presence in solution leads to raise and buffer the system pH to reduce the uptake of fluoride [26]. Overall, the impact of major anions on fluoride adsorption followed the order: $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-$, reflecting the relative affinity of these anions for GRI. A similar trend has also been observed previously for adsorption of fluoride on iron hydroxide based adsorbent [19, 26].

3.7 Desorption of Fluoride

The desorption of fluoride from treated GRI-300 is important for its possible reuse or safe disposal. Since the fluoride adsorption is strongly dependent on pH of the medium, its desorption can be effected by pH variation of the eluent pH. The desorption of fluoride from loaded GRI by shaking with varying concentrations of NaOH for a predetermined optimal time period (2 h) are presented in Fig. 7. It is evident that the release of fluoride at lower pH < 6.0 is less than 5 % and therefore quite safe for disposal at ≤ 6.0. However, the desorption is increased significantly when the pH is increased above ~ 6.0, and more than 65 % of fluoride was released to solution when the pH is increased up to ~ 10. Therefore, alkaline pH is effective for regenerating spent GRI-300. The release of adsorbed fluoride under alkaline pH conditions is presumably due to decrease of protonated surface sites for fluoride binding.

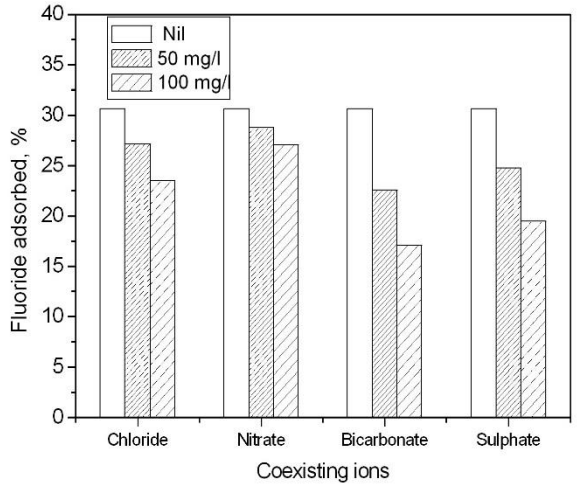

Fig. 6 Effect of coexisting anions on adsorption of fluoride by GRI-300 with initial fluoride, 10 mg/L, pH ~ 6.0 and adsorbent dose, 1 g/L.

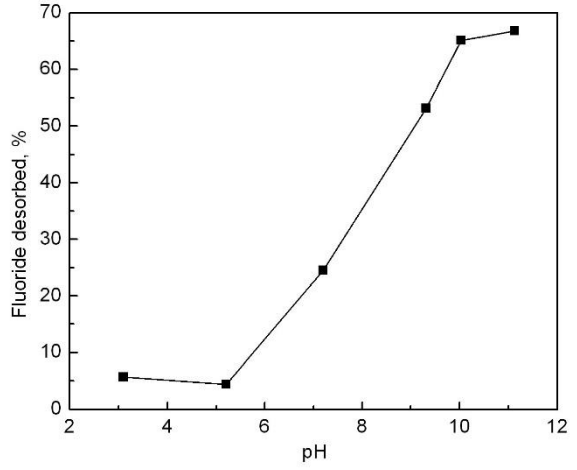

Fig. 7 Desorption of fluoride loaded GRI-300 (fluoride loading 10.4 mg/g)

3.8 Fluoride Removal from Ground Water Sample

In order verify the effectiveness of GRI-300 for removal of fluoride on actual fluoride contaminated water, a typical ground water sample was collected from Kurkutia village of Mayurbhanj district of Orissa and analysed for: F^- (2.43), Cl^- (68.1), SO_4^{2-}(21.2), NO_3^- (16.1), PO_4^{3-} (0.87). Preliminary result shows that stirring one litre of contaminated water with a dose of 5.0 g GRI-300 at pH ~ 6.0 for 2 h reduces the fluoride concentration well below the permissible limit. (< 1.0 mg/L) indicating the potential of GRI for removal of fluoride from water containing fluoride at least at low level.

4. Conclusion

The adsorption of aqueous fluoride by GRI is relatively fast in first 2 h and attained equilibrium within 4-5 h. Maximum adsorption of fluoride is found at pH 4.5-5.5. The adsorption data are well better fitted to Freundlich isotherm indicating that the GRI surface was heterogeneous. The presence of co-existing anions affects the fluoride adsorption and follows the order: $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-$. More than 65 % of adsorbed fluoride can be desorbed by increasing the pH of eluent solution to ~ 10.0. Under optimized condition, GRI-300 can lower the fluoride concentration of actual contaminated water to desired level. The ore can be further exploited for its possible practical use as adsorbent for remediation of anionic pollutant from contaminated water.

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