DEFLUORIDATION USING EGG SHELLS AND RICE HUSK: KINETICS AND EQUILIBRIUM STUDIES

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ABSTRACT

Effects of fluoride in water is both beneficial and detrimental. So fluoride in higher levels must be removed. The present study works with the extraction of fluoride from aqueous solution using natural adsorbents prepared from rice husk and egg shells. Experiments were performed to demonstrate optimal conditions like pH, adsorbent dose and contact period. Egg shells were found to be more effective than rice husk in terms of adsorbent dosage and contact period required. Data from the equilibrium studies was used to understand the order of kinetics and to predict the isotherms of the adsorption process.

Keywords: Fluoride, defluoridation, adsorption, biosrbents, egg shells, rice husk, adsorption isotherms

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1. INTRODUCTION

Fluorine is the 13th most abundant element and is about 0.3 g/Kg of earth's crust. It belongs to the halogen group with atomic number 9 and molecular weight 19. Fluoride having less radius /charge ratio is considered as the most electronegative element with low dissociation energy. This makes fluorine extremely reactive and has a strong affinity to combine in order to produce different compounds with other elements.

Fluorosis is distributed globally and endemic in 25 nations at least. High fluoride concentrations have been recorded in 230 districts in 20 Indian states (after Andhra Pradesh bifurcation in 2014). In India, fluorosis is primarily due to excess fluoride in water except in areas of Gujarat and Uttar Pradesh, where industrial fluorosis is also observed.

In order to protect the generation yet to be born against fluorosis the only best solution would be to provide water with optimal fluoride content. This can be attained by the following methods defluoridation, location of alternative safe sources, supplying water from a distant safe source and minimize industrial fluoride pollution. Of these defluoridation technique is most commonly used. There are many methods of defluoridation like nalgonda technique, activated alumina adsorption, reverse osmosis etc. Each of these techniques have their own advantages and disadvantages. Research is going on to find the low cost and sustainable adsorbent materials.

In the present work natural adsorbents with locally available bio waste such as rice husk and egg shells was developed for fluoride extraction, which can be used as an alternative for various expensive defluoridation techniques. Present study aims at examining the fluoride removal efficiency and adsorption capacity of various natural materials from the water samples collected in the Nalgonda region of Telangana state.

Future Scope: From various studies it is found that the wastewater generated after defluoridation is not being disposed safely. So working on extraction of fluoride from defluoridated sludge will be the solution to this problem.

2. METHODOLOGY

2.1. Equipment and Apparatus

The DR 2700 Portable Spectrophotometer was used for fluoride ion measurement. SPADANS reagent was used in the process. The pH was evaluated using glass electrode with pH/ion meter. Every time measurements were produced, pH meter was gauged by pH calibration buffers.

2.2. Reagents

Reagents like NaF, NaOH, HCl, NaCl, CH₃COOH (glacial), sodium citrate, EDTA, and concentrated H₂SO₄ of analytical grade were used in the entire experiment.

2.3. Preparation of Materials

2.3.1. Rice husk

Rice husk was collected from a local mill and the husk was sieved such that material passing through 300µm and retaining on 150µm was used for the study. Material so obtained after sieving was packed in a container with multiple pores on the surface is kept in muffle furnace at a temperature of 250°C for about 3 hours. The black husk now obtained was termed as RHAC (rice husk activated charcoal).

2.3.1. Egg Shells

From the local region, egg shells were collected and washed with distilled water and then dried. Then the dried shells were grounded and well sieved so that the fraction of material that passes through 300µm and retains at 150µm was used for the research.

2.4. Equilibrium Studies

Equilibrium adsorption studies were conducted with 250 ml of sample water containing 12.5 mg/L of fluoride concentration. Samples were transferred to a conical flask to which 10g of each adsorbent was added. Samples were then shaken at 200 rpm at room temperature for about 2 hours to reach the equilibrium state. After attaining equilibrium sample was filtered using whatman filter paper 1 and was then analyzed for fluoride ion concentration. Adsorption efficiency (%) and equilibrium uptake capacity of each adsorbent was calculated using the following formulas.

$$q_e = \left(\frac{C_o - C_e}{m} \right) v \quad (1)$$

$$\text{removal efficiency \%} = \left(\frac{C_o - C_e}{C_o} \right) 100 \quad (2)$$

Where C_o , C_e are initial and equilibrium fluoride concentrations (mg/L) respectively, m is the mass of the adsorbents used in grams and V is the volume of the solution in litres.

2.5. Preliminary Test

Preliminary test was performed on adsorption efficiency of the adsorbents before undertaking the optimization experiment. For this 250 mL of sample with 12.5 mg/L of fluoride ion concentration was taken in the conical flask to which 10g of each adsorbent was added. Samples were then shaken at a speed of 200 rpm. Then the samples were tested for fluoride concentration at different times (0.5, 1, 1.5, 2, 2.5, 3, 4, 5, 6 hours).

2.6. Optimization of Different Parameters

Optimization was carried out to create those variable workbest by changing one variable while holding others as constants. Various parameters like adsorbent dose, contact time and pH were varied and were optimized.

2.7. Effect of Adsorbent Dosage and Contact Time

Experiments were carried with solutions of different adsorbent dosages varying from 3 to 18g/250 mL of rice husk and treated egg shell powder with initial fluoride concentration of 12.5 ppm at different contact periods ranging from 30 minutes to 6 hours. Adsorbent dosages were based on preliminary studies.

2.8. Effect of pH

The pH of the solution containing 12.5 ppm of initial fluoride concentration was varied from 2-12 using 1N HCL and 1N NaOH. To these solutions 12 g of egg shell powder was added and tested after 90 minutes. In case of adsorbent prepared from rice husk 15 g of it was added and tested after 2 hours. After each experiment residual fluoride was calculated.

2.9. Adsorption Isotherms

Langmuir and Freundlich isotherms were studied in the current discussion using modified adsorbents at room temperature. For plotting isotherms data was obtained from a solution containing initial fluoride concentration of 12.5 mg/L with a series of increasing adsorbent dosages of 3, 6, 9, 12, 15, 18g. Residual fluoride was calculated in each case after attaining equilibrium.

2.9.1. Freundlich Isotherm

Freundlich and Langmuir isotherms are helpful models for understanding adsorption process of various adsorbents. The Freundlich model relates to the adsorbent's surface heterogeneity, while the. Following equation represents the linear form of Freundlich isotherm

$$\log q_e = \log K_f + \left(\frac{1}{n} \right) \log C_e \quad (3)$$

Where q_e is the sum of fluoride ion adsorbed per unit adsorbent mass, mg / g; q_e is the balance adsorbent concentration in solution, mg / L; K_f and n are Friendly constants indicating adsorption efficiency (mg / g) and adsorption frequency, respectively. which were obtained by plotting a linear graph between $\log q_e$ versus $\log C_e$. Values of n greater than 1 indicate favorable sorption.

2.9.2. Langmuir Isotherm

Langmuir model assumes uniform adsorption energies on the surface and no adsorbent transmigration on the surface plane. Linear form of the Langmuir isotherm is given by the following equation

$$\left(\frac{C_e}{q_e}\right) = \frac{1}{Kl \cdot q_m} + \frac{C_e}{q_m} \quad (4)$$

$$Rl = \left(\frac{1}{1 + Kl \cdot C_0}\right) \quad (5)$$

Where q_e is the sum of fluoride ion adsorbed per unit adsorbent mass, mg / g; q_m and Kl are constants of Langmuir representing the power of adsorption and binding strength, respectively. Langmuir constants are determined from the slope and intercept of linear plot of C_e/q_e versus C_e . Rl is the separation factor whose values between 0 and 1 indicates favorable sorption, values greater than 1 indicates unfavorable sorption, value of 0 indicates irreversible sorption and value of 1 indicates linear sorption.

2.10. Adsorption Kinetics

Adsorption kinetics was studied using adsorbent dosage of 3, 6, 9, 12, 15 and 18 g corresponding to the initial fluoride concentration of 12.5 mg/L. At different time intervals of 0.5, 1, 1.5, 2, 2.5, 3, 4, 5 and 6 hours residual fluoride concentrations are measured.

2.10.1. Pseudo First Order Kinetics

$$\log(q_t - q_e) = \log q_e - (k_1 / 2.303)t \quad (6)$$

q_e and q_t are the quantity of fluoride ion adsorbed per unit mass of rice husk or egg shells (mg/g) at equilibrium and at any time respectively. When a straight line is plotted between t and $\log(q_e - q_t)$ slope and intercept of the equation gives $\log(q_e)$ and $k_1/2.303$ respectively where k_1 is the rate constant of first order sorption (min^{-1})

2.10.2. Pseudo Second Order Kinetics

$$t / q_e = 1 / (k_2 \cdot q_e^2) + t / q_e \quad (7)$$

Q_e is the amount of fluoride ion adsorbed per unit mass of adsorbent (mg/g) at equilibrium. When a straight line is plotted between t and t/q_e , slope and intercept of the equation gives $1/q_e$ and $1 / (k_2 \cdot q_e^2)$ respectively where k_2 is the rate constant of second order sorption (min^{-1})

3. RESULTS AND DISCUSSIONS

3.1. Preliminary Study

Different adsorbents have varying adsorption efficiency under similar conditions for the same initial fluoride concentration. It was observed that with adsorbent prepared from egg shells efficiency was about 87% within 3 hours and similarly with adsorbent from rice husk efficiency was about 80% with same contact period. From the study it was clear that both the adsorbents have fluoride ion adsorption potential, but the contact time effects the percentage removal.

Figure 1 Effect of contact time on fluoride removal with initial fluoride concentration of 12.5 ppm and adsorbent dose of 10 grams.

3.2. Adsorbent Dose and Contact Time

From the fig 2 we can say that for both the adsorbents concentration of residual fluoride decreases with the contact time. Over 50% of the initial concentration of fluoride was reduced for all doses of treated rice husk and egg shell powder in the first half an hour. The fluoride removal rate became slow after 30 minutes. This was because at the beginning adsorbent has active sites that are free which resulted in high removal efficiency and later on because of congestion of the active sites, this decreases with increasing contact time. Increase in removal rate of fluoride with increase in adsorbent dose was also observed due to availability of more active sites.

Using treated rice husk about 80% removal efficiency was attained within half an hour with 15 g of adsorbent dosage and with contact time greater than 3 hours fluoride concentration became lower than the limits. Therefore the optimum conditions were considered as contact time of 2 hours and dosage of 15g. In case of egg shell powder 80% efficiency was attained within half an hour using 12 g of dosage and with increase in contact period above 4 hours fluoride concentration has fallen below the prescribed limits. Therefore optimum conditions for egg shell powder were considered as 1.5 hours contact time and 12 g dosage.

Figure 2 Effect of contact time and adsorbent dosage (egg shells) on fluoride removal; initial fluoride concentration of 12.5 ppm.

Figure 3 Effect of contact time and adsorbent dosage (rice husk) on fluoride removal; initial fluoride concentration of 12.5 ppm.

3.3. Effect of pH

From the fig 4 it can be seen that with increase in pH there was a decrease in fluoride removal efficiency. At optimum conditions of dosage and contact time same pattern was observed for both the adsorbents.

Figure 4 Effect of pH on fluoride removal with initial fluoride concentration of 12.5 ppm

3.4. Adsorption Isotherms

The linear form of the Freundlich equilibrium isotherm mode represented the adsorption process well for both the adsorbents with R^2 values of 0.9582 and 0.9814 for egg shells and rice husk respectively; table 1, and the values of n for both the adsorbents was greater than 1 indicating favorable sorption.

Table 1: Freundlich isotherm parameters and correlation coefficients

Adsorbents	n	K_f	R^2
Egg shells	2.15	0.4647	0.9582
Rice husk	1.602	0.1723	0.9814

Table 2 Langmuir isotherm parameters and correlation coefficients

Adsorbents	K_a	q_m	R^2
Egg shells	3.375	0.928	0.8804
Rice husk	0.6395	0.981	0.841

R^2 values of Langmuir isotherm were 0.8804 and 0.841 for egg shells and rice husk respectively and the separation factor R_L was found to be between 0 and 1 ; table 2 indicating favorable sorption.

3.5. Adsorption Kinetics

Compared to the first-order reaction, the pseudo-second order equation fitted experimental data well with and R^2 value approaching to unity; table 4. Based on the correlation coefficients, a second-order reaction pathway is followed by biosorption of fluoride ions by both egg shells and rice husk.

Table 3 Coefficients of pseudo first order reaction and correlation coefficients

Adsorbents	K_2	R^2
Egg shells	2.2189	0.9996
Rice husk	2.2836	0.99994

Table 4 Coefficients of pseudo second order reaction and correlation coefficients

Adsorbents	q_e	K_1	R^2
Egg shells	0.256	0.5071	0.9774
Rice husk	0.205	0.5062	0.9642

4. CONCLUSIONS

This study showed that thermally treated adsorbents made from rice husk and egg shells were ideal for fluoride ion extraction. The operational parameters such as adsorbent dose, contact time and pH were found to have an effect on the adsorption efficiency. All other parameters were found to be same even after defluoridation. Optimum conditions were found to be 12 g of egg shells with contact period of 90 minutes and 15 g of rice husk with contact period of 3 hours. Under optimum conditions adsorbents prepared from rice husk and egg shells displayed the highest efficiency of 90 and 89 percent fluoride extraction, respectively, for an initial concentration of 12.5 mg /L. For both the adsorbents optimum pH was found to be 6. Egg shell was observed to be much more effective than rice husk in terms of time and adsorbent dose required. The adsorption mechanism approaches Freundlich adsorption isotherm in both cases. Adsorption of fluoride by both the adsorbents was best followed by pseudo second order reaction.

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