

Fruit Peel and Shell as a Low-cost Bioadsorbents for Fluoride Removal from Aqueous Solution: A Review

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ABSTRACT: High fluoride content becomes one of the most serious environmental and health problems today. The excessive presence not only affects human beings but also animals and vegetation because of their mobility in aqueous ecosystem, toxicity and non-biodegradability. Removal of fluoride from the aqueous solution is one of the major researches carried out by researchers in the field of environment. Although different methods such as Ion exchange, precipitation, evaporation, membrane filtration and adsorption are used for fluoride removal, adsorption process has attracted attention of many researchers because of low cost, design flexibility, and high efficiency. The present review is focused on the fluoride removal based on the performance of various fruit peel and shell based adsorbents. The objective of this review is to contribute in the search for low cost adsorbents and investigate the parameters that influence the adsorption of fluoride on adsorbents. A summary of available researches has been composed by a range of potentially low-cost fruit peel and shell based adsorbents.

KEYWORDS: Adsorption, Fluoride, Kinetics, Isotherm model

I. INTRODUCTION

Fluoride is a persistent and non-biodegradable pollutant that accumulates in soil, plants, wildlife and human beings [1]. In soil fluoride presents as earth crust (0.6–0.9 %) commonly associated with volcanic activity and gases. It is also present in water and air. On the other hand, in air not large quantities but an average concentration of fluoride ($0.5 \mu\text{g}/\text{m}^3$) is found in the air [2]. Numerous fluoride-containing minerals such as topaz, fluorite, fluorapatite, cryolite, phosphorite, theorapatite, etc. are mostly responsible for fluoride contamination in groundwater and fluoride is also present in geochemical deposit which can be leached out by rainwater [3]. Groundwater forms a major source of drinking water in urban as well as rural areas. According to previous researchers, too much fluoride concentrations have been reported in groundwater in more than 20 developed and developing countries including India where 19 states are facing acute fluoride problems [4]. Fluoride in drinking water is a critical global issue as it can cause dental and skeletal fluorosis when present at levels above the World Health Organization[5] drinking water guideline of 1.5 mg/l. Various defluoridation technologies available to remove fluoride from water, such as Precipitation, Coprecipitation, Nalgonda technique, Adsorption, Electrocoagulation, Electrosorption, Reverse Osmosis, Nanofiltration, Electrodialysis and Donnan dialysis [6], but the adsorption process is generally accepted as the cheapest and most effective method for removal fluoride from water[6].

II. REMOVAL OF DIFFERENT POLLUTANTS BY ADSORPTION

Adsorption is a surface phenomenon with common mechanism for organic and inorganic pollutants removal. When a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure, liquid–solid intermolecular forces of attraction cause some of the solute molecules from the solution to be concentrated or deposited at the solid surface. The solute retained (on the solid surface) in adsorption processes is called adsorbate,

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whereas, the solid on which it is retained is called as an adsorbent. This surface accumulation of adsorbate on adsorbent is called adsorption. This creation of an adsorbed phase having a composition different from that of the bulk fluid phase forms the basis of separation by adsorption technology. In a bulk material, all the bonding requirements (be they ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak Van der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction.

The term pollutant, in a broad sense, refers to a substance/material that changes the natural quality of the environment by physical, chemical, or biological means. Thus, we may have pollution in air, water, and soil. The three main activities that mankind indulges in are domestic, agricultural, and industrial. In all of these activities, a large amount of fresh water is used, which is discharged as wastewater containing different pollutants depending on the type of activity. These may be various inorganic, organic chemicals and biological agents as well as heat and radiations. The removal of these pollutants such as dyes, heavy metals, phenols, pyridine, nitrobenzene, pesticides, biological active agents, dissolved and non-dissolved chemicals, radioactive substances, detergents, polychlorinated biphenyls and other organic hazardous chemicals by different adsorbents (Alumina, Bauxite, Silica gel, Zeolites, ion exchange resins, animal/plant/tree based biosorbents, Carbonaceous materials, natural soils, clays, alloys, bone char, chitosan, geomaterials, agricultural wastes, industrial products/by-products/wastes, metal oxides/hydroxides, nanomaterials, nanocomposit materials, carbon materials, etc.) has been discussed by Gupta V. K., et al., 2009 [7], George z. Kyzas et al. 2014 [8], M. Mohapatra et al. 2009 [9], Vaishali Tomar et al., 2013[10] and Mirna Habuda-stanic et al., 2014 [11] in their review articles.

III. LITERATURE REVIEW ON REMOVAL OF FLUORIDE BY DIFFERENT FRUIT PEEL AND SHELL BASED BIOADSORBENTS

In recent years, many researcher widely studied removal of fluoride from waste water by using fruit peel and shell based inexpensive biosorbents. Activated carbon and chemically modified seed based biomass remains the most widely studied adsorbents, and it has been found to adsorb a variety of materials such as metals, dyes, phenols, and a host of other organic compounds and bio-organisms, and is therefore used for the removal of fluoride from wastewaters by adsorption. The design and operation of the process is convenient and can be handled easily, and the operational costs are therefore comparatively low. As a result, the cost of the adsorbent, and the additional costs of regeneration if required, can be a significant fraction of the overall process costs. These materials have been used as such and sometimes after some minor treatment, and are widely known as low-cost adsorbents. In this review article, a summary of some relevant published data with some of the latest important results and giving a source of up-to-date literature on the adsorption properties of activated carbon and chemically modified fruit peel and shell based biosorbents is presented in Table 1, and some of the results are discussed here.

V. Sivasankar *et al.* [12] prepared carbonized Tamarindus indica fruit shells (V-TIFS) and ammonium carbonate impregnated activated carbon (ACA-TIFS) as a low-cost bioadsorbents. The resulting materials and carbon arising from virgin fruit shells V-TIFS were characterized and assayed as adsorbent for the removal of fluoride anions from groundwater. The fluoride scavenging ability of TIFS carbons was due to naturally dispersed calcium compounds. X-ray diffraction (XRD) showed that TIFS carbon contained a mixture of calcium oxalate and calcium carbonate. Batch studies on the fluoride removal efficiency of TIFS carbons with respect to contact time, pH, initial fluoride concentration, and co-ion interference were conducted. Applicability of various kinetic models (*viz.*, pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich) and sorption isotherms were tested for batch techniques. The fluoride removal capacity of TIFS carbons was found to be 91% and 83% at a pH of 7.05 for V-TIFS and ACA-TIFS carbons, respectively. The practical applicability of TIFS carbons using groundwater samples was approved. The fluoride removal was greater in groundwater without hydrogen carbonate ions than those containing these ions. The characterizations of fluoride unloaded and loaded TIFS carbons were done by SEM and XRD studies.

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Naba Kumar Mondalet al. [13] synthesized Aluminum impregnated coconut fiber ash (AICFA) was used for removal of fluoride from synthetic fluoride solution. The AICFA showed high specific area and strong affinity toward fluoride. Synthesized AICFA was characterized by pH_{ZPC} , FTIR, SEM and XRD studies. Adsorption kinetics indicated that the adsorption equilibrium was reached within 60 min and the adsorption process followed the pseudo-second-order kinetic model better. The Langmuir isotherm model could fit the experimental data well. Thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) change of sorption were also evaluated which indicated that the adsorption process was spontaneous, feasible and exothermic in nature. Furthermore, the coexisting anions had significant effect on fluoride adsorption. Moreover, desorption study with AICFA showed that nearly 98% of fluoride could be leached out at pH 12. Further, the reusable properties of the material supported the possibility of its use commercially.

Tejpratap Singh et al. [14] reported the adsorption of fluoride by using mousambi (*Citrus limetta*) peel and Groundnut (*Arachis hypogaea*) shell. The effects of different and important parameters were studied to find the best operating conditions for maximum removal of fluoride. It also noted the effect of contact time in the removal of fluoride from aqueous solution at neutral pH. Five kinetic models; the pseudo first and second order equations, Pore diffusion, intra - particle diffusion and Elovich equation were selected to follow adsorption process. By fitting of the kinetic data, the dynamics of sorption could be better described by Pseudo-second order model indicating a chemisorptive rate limiting for neem leaves. Though the plots of intra-particle diffusion render straight line with good correlation coefficient, the tail passes through origin in each case. This suggests that the process is 'complex' with more than one mechanism limiting the rate of sorption. The good fitting of kinetic data to pore diffusion and Elovich equation indicate that pore diffusion plays a vital role in controlling the rate of the reactions.

Ganapaty Alagumuthu et al. [15] synthesized zirconium impregnated ground nut shell carbon (ZIGNSC) and tested to determine its capacity and kinetics for fluoride adsorption from aqueous solutions. The analysis of the isotherm equilibrium data using the Langmuir, Freundlich and Redlich–Peterson equations by linear methods showed that the data fitted better with Freundlich model than the other two. Thermodynamic studies revealed that the spontaneous nature of fluoride adsorption with increase of entropy and an endothermic process. The kinetic data obtained for fluoride adsorption on zirconium impregnated ground nut shell carbon (ZIGNSC) obeyed the pseudo-second order equation. The equilibrium time for removal of fluoride was determined to be 180 min. The fluoride saturation capacity of zirconium impregnated ground nut shell carbon is 1.26 mg F⁻/g at room temperature. X-ray diffraction (XRD) studies confirmed the deposition of fluoride on material and Fourier transform infrared (FTIR) studies also showed the involvement of adsorbate on the adsorbent surface in the adsorption interaction. The ZIGNSC provides a cost effective material to the defluoridation problem in the developing countries by its great potential application in the fluoride removal from water.

Y.Hanumantharao et al. [16] reported the surface sorption characteristics of activated carbon prepared from the shells of *Lagenaria Siceraria* towards fluoride has been investigated by varying the operational parameters such as initial concentrations, (1.5-15 mg/L), agitation time (10-70 minutes) and pH (3-10). The experimental isotherms data are analyzed using Langmuir and Freundlich isotherm models. The data is best fitted with the Langmuir isotherm model. The calculated dimensionless separation factor, RL indicates that the adsorption of F⁻ ion onto adsorbent is favorable. First order, pseudo-first order, second order and pseudo-second order kinetic equations and intra particle diffusion and pore diffusion models are used to examine the experimental data. It is found that the pseudo-second order kinetic equation describes the data of F⁻ ion adsorption on adsorbent carbon adequately. The BET surface area pore size distributions, and physicochemical parameters for the adsorbent are obtained by N₂ adsorption at 77 K. Surface morphology is also examined using Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDX) and X-ray Photo Electron Spectroscopy (XPS) before and after adsorption of fluoride ion. The chemical composition, elemental analysis and functional groups on the surface of the active carbon prepared are studied using XRD, and FT-IR techniques.

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Ch. Chakrapani et al. [17] prepared activated carbon adsorbents *viz.*, NCDC, NCMC and NCAC were prepared from the peels of *Citrus documana*, *Citrus medica* and *Citrus aurantifolia* fruits respectively. In the study, adsorption of fluoride onto these activated carbons was investigated. Effect of contact time in the removal of fluoride from aqueous solution at neutral pH was studied. Five kinetic models; the pseudo first- and second-order equations, intraparticle diffusion, pore diffusion and the Elovich equation, were selected to follow adsorption process. Adsorption of fluoride onto adsorbents could be described by pseudo second-order equation. Kinetic parameters; rate constants, equilibrium adsorption capacities and correlation coefficients, for each kinetic equation were calculated and discussed. The good fitting of kinetic data to pore diffusion and Elovich equations indicate that pore diffusion plays a vital role in controlling the rate of the reaction.

Dwivedi Shubha et al. [18] reported the removal of fluoride from synthetic water using mosambi (*Citrus Limetta*) peel powder in a batch reactor. Batch experiments were conducted to study the impacts of agitation time and initial fluoride ion concentrations. The adsorption kinetics is presented well by pseudo second order rate equation and the estimated equilibrium concentration falls within ~ 6 % error limit. Freundlich isotherm gives well prediction of the equilibrium adsorption ($R^2 = 0.996$). The specific uptake increases from 0.089 mg/g to 1.35mg/g with the increase in initial fluoride concentration from 1 mg/L to 20 mg/L. Maximum specific uptake obtained from Langmuir isotherm is found to be 1.82 mg/g. When the initial fluoride concentration is 5mg/L, the removal efficiency of mosambi peel is 82.5% so that the fluoride concentration at the treated water is below the permissible limit.

V. Ramanjaneyulu et al. [19] developed adsorbent from *Tamarindus Indica* (Tamarind) fruit shell to remove fluoride from drinking water. Batch adsorption experiments were undertaken on *Tamarindus Indica fruit shell*. The effect of controlling parameters of adsorption like pH, dose of adsorbent, contact time and initial sorbate concentration on fluoride removal efficiency was studied and optimum values for maximum uptake were found. Tamarind fruit shell exhibited highest fluoride removal efficiency about 85% at pH of 2, initial fluorine concentration of 3 mg/l, contact time of 90 min, adsorbent dosage of 2g/100ml and maintaining temperature of 307 K. The obtained data were fitted to Langmuir and Freundlich isotherms.

Aash Mohammad et al. [20] investigated the feasibility of three low-cost biomass based adsorbents namely: banana peel, groundnut shell and sweet lemon peel for industrial waste water defluoridation at neutral PH range. Action of these adsorbents on fluoride was compared with commercially available adsorbents. It was found to be much better, high removal efficiency at higher concentration (20 mg/l) of fluoride in industrial waste water. The banana peel, groundnut shell and sweet lemon peel removed 94.34, 89.9 and 59.59 % respectively. Contact time for banana peel, groundnut shell, and sweet lemon peel are 60.0, 75.0, and 40 min respectively at doses of 14, 12 and 16 gm/l respectively. Mechanism of adsorption kinetics was found pseudo-second order reaction, and the mechanism of fluoride removal on adsorbents was found to be complex. The surface adsorption as well as intra-particle diffusion contributes to the rate-determining step.

M. Rajan et al. [21] examines the kinetics of fluoride removal from water by the adsorbent zirconium-impregnated walnut-shell carbon (ZIWSC), exploring the mechanisms involved. The dependence of the adsorption of fluoride on the pH of the solution has been studied to achieve the optimum pH value and a better understanding of the adsorption mechanism. The presence of bicarbonate ions in aqueous solution was found to affect the fluoride removal indicating that these anions compete with the sorption of fluoride on adsorbents. The kinetic profile has been modeled using pseudo-first-order model, pseudo-second-order model, and intraparticle diffusion model. The equilibrium adsorption data were fitted reasonably well for Freundlich isotherm model. XRD and SEM patterns of the ZIWSC were recorded to get better insight into the mechanism of adsorption process. The impregnated walnut shell acts as a reasonably good adsorbent for the removal of fluoride from aqueous solution. The optimum pH for removal was found to be 3.0, at which fluoride removal was 94%. The removal increased with the increase in the adsorbate concentration. An increasing equilibrium adsorption capacity with the rise in temperature indicated that the nature of adsorption process is endothermic, which is further supported by the thermodynamic parameters calculated from the Langmuir isotherm at various temperatures. Compared to the various other sorbents reported in the literature, the impregnated walnut shell in

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this study shows very good promise for practical applicability. However, more studies are needed to optimize the system from the regeneration point of view and to investigate the economic aspects.

Evangelina Christina et al. [22] develop a bioadsorbent, by successfully immobilizing saponified orange peel residue (SOPR) in alginate matrix and applying a 3-step modification procedure to enable fluoride sorption from water. Batch equilibrium studies indicate that Langmuir model of isotherm and Pseudo second order rate kinetics were followed with a maximum sorption capacity of 7 mg/g. FTIR studies confirm the involvement of –OH and carbonyl groups in fluoride uptake. The morphological changes are evident in SEM micrographs. Hence electrostatic interaction and ion exchange could be the possible mechanisms by which fluoride ions are removed from water. The developed sorbent could be used effectively for defluoridation in areas where the fluoride concentration exceeds the recommended limit.

Nedunuri Phani Kumar et al. [23] studied defluoridation of water was conducted using Tamarind fruit cover (TNFC) as a natural adsorbent in virgin and acid treated forms. Defluoridation of water was studied under batch equilibrium and column flow experimental conditions. The adsorbents were characterized by FTIR, SEM, Pycnomatic ATC techniques. The effect of experimental variables such as initial concentration of fluoride, effect of pH, contact time, co-ions and amount of adsorbent dosage was evaluated. The study was also extended to real field water samples. The equilibrium data were used to study the kinetics of defluoridation process and also to predict the isotherms applicable to the adsorption process. The maximum monolayer adsorption capacity of virgin TNFC and treated TNFC sorbents as obtained from the Langmuir adsorption isotherm was found to be 4.14 mg/g and 6.11 mg/g of fluoride. The column flow adsorption data were utilized to obtain break through curves.

G. Alagumuthu et al. [24] investigated a zirconium impregnated bioadsorbent for the removal of fluoride ions from aqueous solution. The method is simple and has shown great potential for the removal of fluoride ions. The treatment conditions were optimized: pH value was 7, room temperature and particle size was 53 m. 80.33% salt rejection has been identified in 3 mg/L of 100 ml fluoride using 1.5 mg dosage of adsorbent. The equilibrium sorption data agree reasonably well for Langmuir isotherm model. Sorption dynamic study revealed that the sorption process followed pseudo-second-order equation; the sorption process was complex, both at the boundary of liquid film and intra-particle diffusion contributed to the rate-determining step. The used adsorbents could be regenerated by 96.2% of 2.5% Sodium hydroxide in 180 min.

M.T. Bashir et al. [25] synthesized chemically modified palm kernel-shell based bioadsorbents for removal of fluoride from waste water. Chemically modified palm kernel (CMPKS) showed effective adsorption property with maximum adsorption capacity of 2.35 and 2.01 mg/gat pH 6 and pH 7 respectively. Resin size was observed to be of prime importance in the biosorption process as the optimum removal efficiency with least associated waste generation was observed at a size range of 0.25-0.5 mm. Langmuir and Freundlich isotherms were studied along with pseudo first and second order kinetics models, as well as intraparticle diffusion. Langmuir model and pseudo second order model were observed to be a better fit for this process. Intraparticle diffusion study indicated the probability of chemisorption. SEM showed drastic changes in surface morphology with projections and porous surface. FT-IR analysis also verified the presence of hydroxyl and amine group on the bioadsorbent and consequently verified the applicability of adsorption. Regeneration process showed its long-term and economical use.

John. Bentil et al. [26] prepared activated carbons from coconut shells and palm kernel shells by carbonisation of the residues to obtain chars which were activated at 900⁰C using steam as the activating agent. Analysis of fluoride was done before and after treating water with the derived activated carbons. The water treatment experiment using fluoride as a model pollutant demonstrated that activated carbons prepared from agricultural waste materials have a good potential for fluoride removal. Adsorption of fluoride was also found to be influenced by the type and concentration of other ions in the treated water.

Tej Pratap Singh et al. [27] observed the defluoridation capacity of treated banana peel from industrial waste water in a batch reactor. The effects of time and initial concentration of fluoride on the % removal have been studied. Pseudo second order equation could be used to describe adsorption of fluoride onto adsorbent. Kinetic parameters like

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correlation coefficients, rate constant, equilibrium adsorption capacities for each kinetic equation were determined and discussed. The best fitting of kinetic data to Elovich equation and pore diffusion model indicated that pore diffusion plays a vital role in controlling the rate of the reactions.

Ria Bhaumik et al. [28] synthesized three different adsorbents (untreated, formaldehyde treated and calcium impregnated) of banana peel (*Musa paradisiaca*) dust (BPD) for removal of fluoride from aqueous solution. The effects of operating parameters such as pH, initial concentration, adsorbent dose, contact time, agitation speed and temperature were analysed using response surface methodology. The significance of independent variables and their interactions were tested by the analysis of variance and *t* test statistics. Experimental results revealed that BPD has higher F^- adsorption capacity (17.43, 26.31 and 39.5 mg/g). Fluoride adsorption kinetics followed pseudo-second-order model with high correlation of coefficient value (0.998). On the other hand, thermodynamic data suggest that adsorption is favoured at lower temperature, exothermic in nature and enthalpy driven. The adsorbents were characterized through scanning electron microscope, Fourier transform infrared spectroscopy and point of zero charges (pH_{ZPC}) ranges from pH 6.2–8.2.

Mateso Said et al. [29] studied the removal of fluoride by using chemically treated activated carbon of coconut shell. Batch experiments were carried out to determine the effect of various adsorbent factors such as adsorbent dose, initial pH, particle size and contact time on adsorption process. Adsorption efficiency was observed to increase with decrease in particle size, the highest efficiency recorded was 68.2 and 65.9% for field and synthetic water respectively when particle size less than 150μ of coconut shells activated carbon were used. Adsorption was observed to be favoured by pH in acidic range and the maximum efficiency of 58.4% was recorded at pH of 2.0 and particle sizes between 4.18–2.36mm. The pH of the effluent was lowered to acidic range which necessitates further treatment of the effluent or coupling with other materials for pH elevation before use. Adsorption increases with adsorbent dose hence at a smaller influent concentration; the required standard of 1.5mg/l can be met. Equilibrium isotherms have been analysed using Langmuir and Freundlich isotherm models, and both of the models fit to explain the adsorption behaviour of fluoride ions onto Coconut shell activated carbons.

G. Anusha et al. [30] conducted a batch study adsorption by adsorption process using activated carbon prepared from Bale fruit (*Limonia acidissima*) shell as adsorbent and the removal efficiency is determined by optimizing the parameters such as dosage, time, pH and concentration. The maximum removal efficiency was found to be more than 63%. This experimental study proves to be an economical method of fluoride removal since the developed product is a waste product.

L.A. Ramirez-Montoya et al. [31] presented a comparative study of fluoride removal using samples of carbons obtained from single carbonization from pecan nut shells and plum kernels and carbons obtained by impregnation of these wastes, prior to their carbonization, with a calcium acetate solution. The impregnation step was determinant for increasing the ability of carbons to remove fluoride anions from water of carbons prepared from both precursors. The intrinsic calcium content of the precursors left a footprint in the process, with carbons prepared from the higher calcium content precursor (i.e., pecan nut shells) always performing better than the plum kernel carbon counterpart. Outstanding fluoride retention abilities (from 0.5 to 2.5 mg of fluoride adsorbed per gram of carbon) were obtained if pecan nut shells are impregnated with a calcium solution of 3151 mg/L and carbonized at $800^{\circ}C$ (sample denominated IC-PN-25). These results can be associated with the calcium compounds founded in IC-PN-25 which are CaO and CaCO₃, according with the X-ray results. Furthermore, dynamic adsorption studies were carried out using beds of carbon denominated IC-PN-25. Reasonably high (0.4) filter usage ratios were obtained in such on-column adsorption studies. Finally, different models were used to fit batch and dynamic adsorption data, with Sips and Yan models fitting better the equilibrium isotherm and breakthrough curve data, respectively, than others.

Rajan Mariappan et al. [32] prepared chemically activated cotton nut shell carbons (CTNSCs) by different chemicals and they were used for the removal of fluoride from aqueous solution. Effects of adsorption time, adsorbent dose, pH of the solution, initial concentration of fluoride, and temperature of the solution were studied with equilibrium,

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thermodynamics and kinetics of the adsorption process by various CTNSC adsorbents. It showed that the chemically activated CTNSCs can effectively remove fluoride from the solution. The adsorption equilibrium data correlate well with the Freundlich isotherm model. The adsorption of fluoride by the chemically activated CTNSC is spontaneous and endothermic in nature. The pseudo first order, pseudo second order and intra particle diffusion kinetic models were applied to test the experimental data. The pseudo second order kinetic model provided a better correlation of the experimental data in comparison with the pseudo-first-order and intra particle diffusion models. A mechanism of fluoride adsorption associating chemisorption and physisorption processes is presented allowing the discussion of the variations in adsorption behavior between these materials in terms of specific surface area and porosity. These data suggest that chemically activated CTNSCs are promising materials for fluoride sorption.

Supata Chakrabarty et al. [33] studied the effectiveness of betel nut coir charcoal as a potential adsorbent for defluoridation of synthetic aqueous solution following batch method of operation. The efficiency of the adsorbent was measured at different temperature settings with respect to initial fluoride concentration, contact time, and pH of the solution. The process achieved equilibrium at 180 minutes with maximum defluoridation efficiency of 92%. The isotherm can be conformed to both Langmuir and Freundlich model at different temperature. The process follows pseudo second order rate with both boundary layer effect and pore diffusion mechanism.

IV. CONCLUSION

This review shows that adsorption process has great potential for the elimination of fluoride from Industrial wastewater using fruit peel and shell based low cost adsorbents. During this review article, an assay has been made to specialize in the recent developments associated with fluoride removal by low-cost adsorbents utilizing fruit peel and shell based bioadsorbents. More studies should be carried out for low-cost adsorption process to promote large scale use of non-conventional adsorbents. Low cost adsorbents should be used to minimize cost and maximize heavy metal removal efficiency.

Table 1. : Comparative details of various fruit peel and shell based adsorbents for removal of fluoride.

Adsorbents	pH range	*Temp. Range (K)	Contact Time range (Min)	Concentration range (mg/L)	® Isotherm model used	# Kinetics model used	Maximum % Removal	Maximum adsorption capacity (mg/g)	Surface area (m ² /g)	Reference
Untreated <i>Tamarindus indica</i> fruit shell activated carbon (V-TIFS)	4-12	298 ± 2	30	2-8	L, F, T, D-R	PF, PS, ID, E	91	--	--	[12]
Ammonium carbonate impregnated <i>Tamarindus indica</i> fruit shell activated carbon (ACA-TIFS)	4-12	298 ± 2	30	2-8	L, F, T, D-R	PF, PS, ID, E	83	--	--	[12]
Aluminum impregnated coconut fiber activated carbon (AICFA)	4-10	315-375	5-70	1-10	L, F, D-R	PF, PS, ID	93.08	3.192	26.3	[13]
Mousambi (<i>Citrus limetta</i>) peel	7	302 ± 1	10-60	--	--	PF, PS, ID, BPD, E	--	1.915	--	[14]
Groundnut (<i>Arachis hypogaea</i>) shell	7	302 ± 1	10-60	--	--	PF, PS, ID, BPD, E	--	1.15	--	[14]
Zirconium impregnated groundnut shell (<i>Arachis hypogaea</i>) carbon	3-12	303-333	60-210	2-10	L, F, R-P	PF, PS, ID	84	1.26	2.12	[15]
Activated carbon of <i>Lagenaria Siceraria</i> shell	3-10	303 ± 1	10-70	1.5-15	L, F	PF, PS, ID, BPD	100	--	198.50	[16]

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Activated carbon of <i>Citrus documana</i> fruit peel (NCDC)	7	298 ± 2	5-50	5	--	PF, PS, ID, BPD, E	--	--	--	[17]
Activated carbon of <i>Citrus medica</i> fruit peel (NMC)	7	298 ± 2	5-50	5	--	PF, PS, ID, BPD, E	--	--	--	[17]
Activated carbon of <i>Citrus aurantifolia</i> fruit peel (NCAC)	7	298 ± 2	5-50	5	--	PF, PS, ID, BPD, E	--	--	--	[17]
Untreated Mousambi (<i>Citrus limetta</i>) fruit peel	7	303	5-60	1-20	L, F, T	PF, PS, ID, E	82.5	1.82	--	[18]
Acid and alkali treated <i>Tamarindus Indica</i> fruit shell	2-10	307	30-150	3-15	L, F	--	85	--	--	[19]
Acid treated Banana peels	2-12	303 ± 1	10-90	10-30	L, F, T	PF, PS, ID	94.34	1.340	--	[20]
Untreated Sweet Lemon Peel	2-12	303 ± 1	10-90	10-30	L, F, T	PF, PS, ID	59.59	0.744	--	[20]
Untreated Groundnut shells	2-12	303 ± 1	10-90	10-30	L, F, T	PF, PS, ID	89.9	1.498	--	[20]
Zirconium impregnated Walnut Shell Carbon	3-12	303-333	20-180	2-10	L, F, T	PF, PS, ID	94	3.53	--	[21]
Saponified orange peel residue (SOPR)	3-9	298-310	10-80	10-50	L, F	PF, PS	--	7	--	[22]
Adsorbents	pH range	*Temp. Range (K)	Contact Time range (Min)	Concentration range (mg/L)	@Isotherm model used	#Kinetics model used	Maximum % Removal	Maximum adsorption capacity (mg/g)	Surface area (m ² /g)	Reference
Untreated Tamarind fruit cover (Virgin TNFC)	1-8	298 ± 1	20-120	5-25	L, F	PF, PS, ID	--	4.14	--	[23]
Acid treated Tamarind fruit cover (Treated TNFC)	1-8	298 ± 1	20-120	5-25	L, F	PF, PS, ID	--	6.11	--	[23]
Zirconium impregnated cashew nut shell carbon	7	303-333	60-210	2-10	L, F, R-P	PF, PS, ID	80.33	1.95	--	[24]
Chemically modified palm kernel-shell	3-9	301 ± 2	5-90	2.5-15	L, F	PF, PS, ID	83.4	2.35	--	[25]
Untreated Banana peel (Musa paradisiaca)dust (BPD-1)	2-10	313-343	10-240	1.5-15	L, F, T, D-R	PF, PS, ID	95.43	17.43	312.3	[28]
Formaldehyde treated Banana peel (Musa paradisiaca) (BPD-2)	2-10	313-343	10-240	1.5-15	L, F, T, D-R	PF, PS, ID	96.39	26.31	884.7	[28]
Calcium impregnated Banana peel (Musa paradisiaca) (BPD-3)	2-10	313-343	10-240	1.5-15	L, F, T, D-R	PF, PS, ID	98.19	39.5	912.3	[28]
Betel nut coir charcoal	2-8	298-328	15-180	2-10	L, F	PF, PS, ID	92	--	--	[33]

* RT-Room temperature.

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@ L: Langmuir, F: Freundlich, T: Tempkin, D-R : Dubinin-Radushkevich , R-P : Redlich–Peterson, BET: Brunauer–Emmett–Teller isotherms.

PF: Pseudo first order, PS: Pseudo second order, ID: Intraparticle diffusion model, E: Elovich model, BPD: Bangham's Pore diffusion kinetic models

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