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Fluoride removal from drinking water (Metlaoui, Tunisia) using untreated and treated natural clays

Short title: Fluoride removal from water using untreated and treated natural clays

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Abstract

BACKGROUND

Fluorosis is an endemic disease due to an excess of fluoride intake via drinking water. In some regions of the world, removing fluoride from drinking water is a severe problem that is still to be solved. The present study focuses on the use of a natural clay to reduce fluoride concentration in Tunisian-contaminated drinking water under relevant working conditions.

RESULTS

The adsorption experiments were performed in batches using a fluoride aqueous solution. The Box-Behnken model design was used to define the working conditions in which three factors were controlled: clay dosage, contact time and agitation speed. The fixed parameters were the initial fluoride concentration and water pH as observed in Metlaoui, Tunisia in 2021, and experiments were performed at room temperature. Results show that 4 g·50 mL^{-1} of clay dosage, 10 min of contact time and 280 rpm of agitation speed could provide 51% fluoride removal using an untreated natural clay. Then, different adsorbents based on this clay were synthesized (chitosan-clay, $C_6H_{17}NO_3Si$-clay and thermally treated clays purified with different methods) and tested using the same approach. Among the adsorbents tested, the thermally treated purified clays were the most effective in removing fluoride under ambient conditions with a fluoride removal of 97.5%. Tests performed on drinking water showed that the safety fluoride concentration could be achieved without modifications of the water pH.

CONCLUSION

The thermally treated clays suggested in this study were effective for fluoride removal under relevant conditions, which can pave the way for future field applications.

Keywords

Biopolymer-clay composites; Thermally treated clay; Box-Behnken design; Water defluoridation

1   Introduction

Fluorine is the 13th most abundant element in the earth's crust.[1] It occurs in the environment as the ionic form of fluoride (F$^-$) due to its high electronegativity.[1] Soils that have minerals like fluorite (CaF_2), cryolite (Na_3AlF_6) and fluorapatite ($Ca_5(PO_4)_3F$) have high fluoride content and represent the major natural source of fluoride in the environment.[1, 2] Fluoride can also originate from different anthropogenic sources, mainly industrial aerosols (exp.: burning coal and the emission of fluoride particulate from steel,… etc.).[2] Different complex mechanisms lead to incorporating fluoride into the hydrosphere, atmosphere and biosphere. Briefly, fluoride can be incorporated into the hydrosphere through the atmosphere and the dissolution of the minerals, and into the atmosphere through evapo-transpiration of the water

and the plants.[2] Fluoride can be incorporated into the biosphere through the hydrosphere, atmosphere and soils.[2]

Fluoride is a mineral that can have both beneficial and detrimental effects on human health. When taken at an adequate dose, fluoride helps to prevent tooth decay.[1] However, the daily intake of excess fluoride causes many harmful effects, essentially dental and skeletal fluorosis.[2, 3] Alzheimer, sterility, thyroid disorder, cancer and more can result from excess fluoride consumption.[3, 4] Humans are exposed almost daily to fluoride uptake. Fluoride can be present at varied levels in food items (fish and date,… etc.), beverages (tea and energy drinks,… ect.), air and drinking water.[5-8] In the literature, some studies assessed the estimated daily intake (EDI) and the hazard quotient (HQ) of fluoride present in different drinks.[1, 5, 6, 7, 8] It was shown that EDI and HQ of fluoride are much higher via the consumption of contaminated drinking water than for other exposure routes. It is considered that drinking water is the primary source of fluoride uptake in the body.[2, 9] Currently, the World Health Organization (WHO) sets the safety limit of fluoride in drinking water to $1.5 \ mg \cdot L^{-1}$.[10] Some countries around the world are confronted with fluoride-contaminated drinking water resources. It is estimated that 300 million persons suffer from fluorosis in China, 64.6 million in India, 20.3 million in Africa, 4.1 million in Canada and so forth.[2] To date, 25 % of the Tunisian population is at risk of fluorosis due to the high fluoride levels detected in different areas.[11] The Gafsa phosphate basin of Tunisia is known for dental fluorosis occurrence which is characterized by teeth discoloration.

Water defluoridation remains to this day a challenge. Conventional techniques such as electrochemical, adsorption, ion exchange, coagulation and membrane processes have been studied in order to reduce fluoride in water.[12] Among them, adsorption is highly recommended because of the large number of available adsorbents (natural and synthetic), the ease of treatment design and its environment-friendly perspective.[13] In recent years, several efforts have been made in order to develop practical adsorbents. Modified pumice,[14] Moringa oleifera seed ash,[15] Padina sanctae crucis algae,[16] cuttlebone,[17] Bauxite,[18] decyltrimethylammonium bromide/H_2O_2 solution-treated organic matter rich clay,[19] Prosopis cineraria and Syzygium cumini leaves,[20] $MgFe_2O_4$ – chitosan – CaAl composite,[13] washed and dried montmorillonite[4] and 3D porous Ca-modified Mg-Zr mixed metal oxides,[21] are some of the adsorbents investigated. A major difficulty in achieving high percentages of fluoride removal is the need to modify water pH which has outcomes for potability.[12] The

effectiveness of developed adsorbents with natural water and the impact of the treatment on the resulting water quality (particularly pH, major cations and anions) is poorly studied.

Clay is a ubiquitous, inexpensive, non-polluting natural resource and was chosen as a fluoride adsorbent for this study. [22-24] As far as we know, the adsorption optimization of fluoride on natural clays is usually studied by modifying one variable at a time. The response surface methodology (RSM) is an empirical mathematical tool used to quantify the individual and combined effects of different independent factors (variables) on a response (result).[25] In this study, the RSM, through the Box-Behnken (BB) design, was used. Three factors were controlled, namely: clay dosage, contact time and agitation speed at fixed fluoride concentration as observed in Tunisian contaminated drinking water (for the city of Metlaoui), without adjusting water pH and at room temperature. Different adsorbents based on a natural clay were synthesized and characterized by X-ray diffraction (XRD).They were tested for their efficiency in removing fluoride and compared with each other. Tests on the actual water were performed; and pH and the major cations and anions were measured before and after defluoridation.

2 Materials and methods

2.1 Materials

The selected natural clay was from Jebel Haïdoudi which is situated in southeastern Tunisia. The clay is composed of an interstratified smectite (75%)-illite and a small proportion of kaolinite.[26, 27] The smectite fraction is a naturally sodic beidellite.[26, 27] The average structural formula of the clay is $(Si_{6.9478} Al_{1.052})^{IV}(Al_{2.651} Fe_{0.917} Mg_{0.433} Ti_{0.098} Mn_{0.002})^{VI} O_{20} (OH)_4 Na_{0.643} Ca_{0.039} K_{0.285})$.[27] Sodium chloride (NaCl), chitosan (2-Amino-2-deoxy-(1→4)-β-D-glucopyranan Poly-(1,4-β-D-glucopyranosamine) and (3-Aminopropyl)trimethoxysilane $(C_6H_{17}NO_3Si)$ were purchased from Sigma-Aldrich. Disodium carbonate (Na_2CO_3) and sodium fluoride (NaF) were purchased from Fisher.

The mineralogical structure of the adsorbents was identified by powder X-ray diffraction (XRD) using Bruker D8 advance diffractometer with Cu Kα radiation ($\lambda = 1.54$ Å). On the patterns, results are given in terms of reticular distance (d_{hkl}) using the well-known Bragg formula. Fluoride (F^-), chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}) and phosphate (PO_4^{3-}) concentrations in the water were analyzed using Integrion HPIC ion chromatography.

Calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+) and potassium (K^+) concentrations were analyzed using an Agilent 5110 dual view inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The pH was measured using Fisher Scientific Accumet AB150 pH meter.

2.2 Adsorbents syntheses

2.2.1 Natural clay

The natural clay was grounded using an automatic agate grinder for 20 minutes and sieved at 100 μm. The raw clay was referred to as HR.

2.2.2 Purified clays and biopolymer-clay composites

Purified clays

The purification was performed using two different methods. First, the purification was carried out using NaCl following the classical method.[28] Briefly, this involved three main steps: i) cationic exchange ii) washing with demineralized water and iii) dialysis. The obtained material was referred to as HP.

Second, the purification was carried out using Na_2CO_3 instead of NaCl. For this purpose, 7.5% w/v suspension of HR clay was prepared in a Na_2CO_3 solution (0.02 M) and was agitated for 24 hours. The resulting suspension was then submitted to three cycles of agitation in demineralized water followed by centrifugation at 6000 rpm for 30 minutes. After centrifugation, the pellet was recovered and was submitted to fractionation by sedimentation for about 2 days. After that, the top layer of the sediment was recovered and then dried in oven at 60 °C, ground and sieved at 75 μm. The material obtained was referred to as HP_0.

Chitosan-clay composite

The chitosan stock solution was prepared by adding 402.5 mg of chitosan in 12.5 mL of acetic acid (1% v/v) with subsequent agitation for 4 hours. The solution was then mixed with an HP aqueous suspension (2% w/v) and the mixture was agitated for 2 hours.[29] The resulting suspension was then centrifuged at 3500 rpm for 15 minutes and the pellet was dried in an oven at 60 °C, grounded and sieved at 75 μm. The obtained material was referred to as chitosan-HP.

Silane-clay composite

A volume of 2 mL of $C_6H_{17}NO_3Si$ was diluted in 50 mL of ethanol and then the solution was added to an HP aqueous suspension (1% w/v). The mixture was agitated for 72 hours and was submitted to four cycles of agitation in ethanol followed by centrifugation at 3500 rpm for 15 minutes.[30] After the final centrifugation, the pellet was dried in an oven at 60 °C, grounded and sieved at 75 μm. The obtained material was referred to as $C_6H_{17}NO_3Si$-HP.

2.2.3 Thermal treatment

Heated purified clays

The purified clay (HP) was heated at 500 °C for 4 hours using a muffle furnace with a heating rate of 12.5 °C·min^{-1}. The material obtained was referred to as HHP.

The purified clay (HP_0) was also heated at 500 °C for 4 hours at a heating rate of 12.5 °C·min^{-1} and the final product was referred to as HHP_0.

Heated washed clay

The heated washed clay (HWC) was prepared through six successive steps:[31] i) agitation of an HR aqueous suspension (20% w/v) for 2 hours, ii) sedimentation of the suspension for about 4 days, iii) intense washing of the recovered top layer of the sediment by agitation in demineralized water for 30 minutes followed by centrifugation at 6000 rpm for 30 minutes, iv) sedimentation of the pellet for about 2 days to ensure the disappearance of the impurities, v) drying in an oven at 60 °C, grinding and sieving at 75 μm. The obtained clay was referred to as WC. Sixthly, the WC was heated at 500 °C for 4 hours at a heating rate of 12.5 °C·min^{-1}. The obtained adsorbent was referred to as HWC.

2.3 Adsorption

2.3.1 Experiments

Adsorption experiments were carried out in batches. At each run, a fixed amount of a given adsorbent was agitated with a 50 mL of fluoride aqueous solution into a Nalgene flask. The fluoride solution was prepared by dissolving the required amount of NaF in demineralized water. After reaching the desired contact time, the suspension was centrifuged at 6000 rpm for about 30 minutes and the supernatant water was recovered to determine the final fluoride concentration.

First, the BB design was employed for preliminary experiments using the raw clay HR in order to determine the working parameter range of values, i.e.: clay dosage (g·mL^{-1}), contact time (min) and agitation speed (rpm) while fixing other exposure conditions, i.e.: initial fluoride concentration close to that observed in the Tunisian fluoride contaminated drinking water (3.37 mg·L^{-1}), without adjusting water pH (5.5) and at room temperature (22 °C). Second, the developed adsorbents were tested under the estimated BB parameter values and compared with each other.

Third, the tests to determine the best adsorbents were performed on the drinking water collected in 2021 from the city of Metlaoui, Tunisia.

2.3.2 Box-Behnken design

The BB design is shown in Table 1. The design includes three factors (clay dosage (X_1), contact time (X_2) and agitation speed (X_3)). The percent of the fluoride removal was examined as a response. The BB design involves three levels per factor which are decomposed of low, center and high levels and generally expressed in the form of coded values as -1, 0 and 1, respectively.[25] The experimental levels of the factors were also illustrated in Table 1.The BB design was composed of 15 experiments including three replicates at the center.

The observed percent of the fluoride removal was calculated according to equation 1:

$$F\% = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

where F% is the observed response; C_i and C_f (mg·L^{-1}) are the initial and final fluoride concentrations, respectively.

The predicted percent of fluoride removal could be estimated empirically by a second-order polynomial as described in equation 2:

$$Y = a_0 + \sum a_i X_i + \sum a_{ii} X_i^2 + \sum a_{ij} X_i X_j + \varepsilon \qquad (2)$$

where Y is the predicted response; X_i and X_j are the levels of the factors; a_0 is the constant coefficient of the model; a_i, a_{ii} and a_{ij} are the model coefficients that designate the linear, quadratic and linear by linear effects of the factors, respectively; ε is the error.[32]

The fitness of the BB model for the fluoride/HR adsorption system was justified mainly by the analysis of the variance (ANOVA). The BB design and its corresponding mathematical

and statistical significance were determined using NemrodW software (version 2000). The 3D response surfaces plots were prepared using the same software.

3 Results and discussion

3.1 X-ray diffraction of the developed adsorbents

XRD patterns for the natural clay (HR), the purified clay (HP) and the biopolymer-clay composites are shown in Figure 1.The HR XRD pattern indicates that the non-clay fractions are gypsum (7.59 Å) and quartz (3.34 Å).[33, 34] These peaks disappeared after clay purification (HP pattern). The peak at 12.82 Å corresponds to the d_{001} of a homoionic sodic beidellite.[26] The chitosan-HP composite pattern shows different novel peaks, suggesting the synthesis of the composite. In fact, chitosan contains many hydroxyl and amine groups in its structure, which can be linked together through strong hydrogen bonds.[13] This led probably to the appearance of novel crystals.[13] The $C_6H_{17}NO_3Si$ composite pattern shows a peak at 10.52 Å which corresponds probably to the d_{002} of the beidellite. That is in accord with results obtained in a similar study, suggesting the successful synthesis of the $C_6H_{17}NO_3Si$-HP composite.[30]

XRD patterns of the thermally treated clays are shown in Figure 2. The XRD patterns for the samples before heating are also illustrated, i.e., the purified clay (HP), the purified clay using Na_2CO_3 (HP$_0$) and the washed clay (WC).The HP pattern shows a peak at 12.82 Å. After heating, the peak decreased to 10.15 Å (HHP pattern). That indicates the collapse of the layers following the heating process. The HP$_0$ pattern shows a peak at 12.66 Å. The peak of quartz persisted (3.34 Å). After heating, the peak decreased from 12.66 to 10.08 Å (HHP$_0$ pattern). The WC pattern shows a peak at 15.33 Å; such a peak is due to a partial dealumination of the beidellite following the intense washing done during the process.[31] After heating, the peak decreased to 10.15 Å (HWC pattern).

3.2 Adsorption

3.2.1 Box-Behnken statistical analysis

Box-Behnken model fitness

The observed results of the BB design are shown in Table 1. The significance of the model coefficients is shown in Table 2. The coefficient a_1 with a very low p-value of <0.0001 is highly statistically significant. The coefficient a_2^2 with a p-value of 0.0179 is statistically significant. The coefficients with p-value >0.05 are statistically insignificant. An analysis of variance (ANOVA) was used to predict the sources of the variation in the responses either from the error or the effects of the factors.[32] The results of the ANOVA are shown in Table 3. The F-value of the model is 34.0451, which is higher than the standard F-value obtained from the distribution table at a 95 % confidence level (4.77). The model p-value of 0.00124 is lower than 0.05, indicating that the model F-value is significant. The variation of the responses is well due to the effects of the factors.[32] The lack of fit F-value of 3.3031 is smaller than the standard F-value at a 95% confidence level (19.2). The lack of fit p-value of 0.241 is higher than 0.05, indicating that the lack of fit F-value is not significant. The not significant lack of fit validated the BB model.[25, 35, 36] The normality of the residuals was verified and the normal probability plot is shown in Figure 3. As can be seen, the data points are reasonably aligned which indicated that the residuals are normally distributed.[13] The coefficient of determination (R^2) of 0.984 is close to unity, indicating the goodness of fit of the BB model. The predicted R^2 of 0.780 and the adjusted R^2 of 0.955 are within about 0.2 of each other, indicating that they are in good agreement.[35] These statistical results justify the fitness of the BB model for the fluoride/natural clay adsorption system. The BB model was then used to estimate the working parameter values.

Interpretation

The BB model revealed that the coefficient a_1 is highly statistically significant. This indicates the strong relationship between fluoride removal efficiency and clay dose. It is interesting to note that this outcome only applies in the dose range studied of 0.5 - 4 g·50 mL^{-1}. At least three other studies also reported considerable effects on fluoride removal by increasing doses of *Ziziphus* leaves, pumice and cuttlefish bone, respectively.[37, 17, 38] In contrast, Tangestani et al. reported an almost constant fluoride removal efficiency by increasing *Rhizopus oryzae* fungal biomass from 0.25 to 2 g·L^{-1}.[39] Keshtkar et al. investigated the fluoride removal efficiency by increasing the dose of *Prosopis cineraria* leaves from 1 to 25 g·L^{-1}.[20] Fluoride removal increased with the adsorbent dose from 1 to 10 g·L^{-1} followed by a plateau.

The contact time and the agitation speed in the ranges of 10 - 1440 min and 60 - 500 rpm, respectively, do not show any statistically significant effects on fluoride removal. A similar

result has been observed in a previous study. Charbti et al. showed negligible effect on fluoride removal by increasing contact time from 1 to 120 min by using treated clay.[31] Goswami and Purkait only observed a slight decrease in removal efficiency from 85.8 to 72.2 % by increasing the agitation speed from 500 to 1500 rpm by using pyrophillite.[40]

The combined effects between the input factors are statistically insignificant, suggesting the dominant effect of the clay dosage in such a system. Various studies examined the fluoride removal efficiency by varying the adsorbent dose effect at different contact times and vice versa. It was often shown that the adsorbent dose is independent of the contact time on fluoride removal. Keshtkar et al. observed an equilibrium time of 60 min by using *Syzygium cumini* leaves whatever the dose used, either $1 - 25$ g·L^{-1}.[20] Tangestani et al. reported an equilibrium time of 30 min by varying the adsorbent dose from 0.25 to 2 g·L^{-1} of *Rhizopus oryzae* fungal biomass.[39] In contrast, Singh Solanki et al. reported significant combined clay dose – contact time effect on fluoride removal by using Fe/Al/Ca based adsorbent.[36]

The working parameter values are revealed from the 3D response surfaces plots (Fig. 4a-c). The latter show the combined effects between the clay dosage (X_1) – contact time (X_2) at fixed agitation speed (X_3) in different levels (low (Fig. 4a), center (Fig. 4b) and high (Fig. 4c) levels). It can be clearly observed that the fluoride removal increases directly with the clay dosage and the maximum fluoride removal is reached with high levels of clay dosage (Fig. 4a-c). Figure 4c shows that when the level of the agitation speed is high, it should operate with low levels of contact time to reach the maximal fluoride removal (red zone in Fig. 4c). Such condition is observed neither for the low-(Fig. 4a) nor the mid-(Fig. 4b) levels of agitation speed. The slight curvature observed in the plots depends probably to the minor quadratic effect of the contact time.

According to the BB model results, a high level of clay dosage (4 g·50 mL^{-1}), a low level of contact time (10 min) and a mid-level of agitation speed (280 rpm) are selected for the subsequent adsorption experiments.

3.2.2 Adsorbents performance

The developed adsorbents, i.e. the biopolymer-clay composites (chitosan-HP and $C_6H_{17}NO_3Si$-HP) and the thermally treated clays (heated purified clay (HHP), heated washed clay (HWC) and heated purified clay using Na_2CO_3 (HHP$_0$)), are compared with each other under the BB estimated variables. The results are shown in Table 4. The thermally treated

clays gave better results than the biopolymer-clay composites while the chitosan-HP was not found to be an effective fluoride adsorbent. This may be due to the negative charge of the adsorbent since the amine groups in the chitosan structure have not probably been protonated at the working pH and/or the crystalline character of the chitosan in the composite. The $C_6H_{17}NO_3Si$-HP also seems unsuccessful in fluoride removal since OH^- tends probably to compete with F^- for active sites.[24, 41] As can be seen in Table 4, the final pH of the treated water with the silylated clay is 9.79 due probably to the amine groups of the grafted silane. The heated purified clay (HHP), heated washed clay (HWC) and heated purified clay using Na_2CO_3 (HHP$_0$) have F% of 51.5, 89.7 and 97.5%, respectively. Interestingly, by using WC, HP and HP$_0$ as adsorbents (clays before heating), the residual fluoride concentration in the aqueous solution could not be detected. That was probably due to the clay's swelling property and the formation of stable suspensions in water which were difficult to pellet during the centrifugation. The thermal treatment of the clay seems very effective for fluoride adsorption under normal operating conditions. In fact, the heating process creates vacancy sites of OH^- in the octahedral sheets which could be active adsorption sites for F^-.[31, 42] When comparing the heated purified clay (HHP), heated washed clay (HWC) and heated purified clay using Na_2CO_3 (HHP$_0$), the latter shows the best F%. This may be due to the departure of the CO_3^{2-} from the purified clay after heating and the creation of additional active sites for F^-.[43] The heated washed clay (HWC) is more effective than the heated purified clay (HHP). Such a result confirms a previous study that suggested that the dealumination of the clay could create active sites for F^-.[31] Figure 5 represents the proposed conceptual mechanism of fluoride adsorption on the heated washed clay (HWC). This conceptual model is based on a previous detailed study of the fluoride adsorption mechanism on HWC which was done using solid-state nuclear magnetic resonance spectrometry.[31]

3.2.3 Comparison between adsorbents used in this study and other adsorbents suggested in the literature

Table 5 presents different fluoride adsorbents suggested in the literature compared with those developed in this study. Here, the results of the percent of fluoride removal F (%) for adsorbents tested without adjusting water pH (5.5) or at pH = 7 were summarized. The data were obtained from tests on fluoride synthetic water. Most of the adsorbents are potent under well-determined operations conditions. It seems that Moringa oleifera ash, Padina sanctae crucis algae and the adsorbents developed in this study have a lower operating time than the others listed. This could be an advantage for their applicability in the field.

4   Applicability on natural water

The heated washed clay (HWC) and the heated purified clay using Na_2CO_3 (HHP_0) were tested on Tunisian drinking water. The working parameters values were the pH of the drinking water (7.5), clay dosage (1 g·50 mL^{-1}), contact time (10 min), agitation speed (280 rpm) and room temperature (20 ± 2 °C). Note that we reduced the clay dosage for experiments using natural water. The physical-chemical analysis results of the water before and after fluoride adsorption are given in Table 6. As can be seen, F$^-$ can be reduced from 2.51 to1.15 and 1.51 mg·L^{-1} using HWC and HHP_0, respectively. Contrary to the results observed using a synthetic fluoride solution, HWC seems more effective than HHP_0 using natural water. That is due to the cationic exchange capacity of the clay and the positive correlation between Na$^+$ and F$^-$ in water.[2] As shown in Table 6, using HHP_0, Na$^+$ concentration was increased from 318 to 413 mg·L^{-1} and Ca^{2+} concentration was decreased from 213 to 178 mg·L^{-1}. And using HWC, Na$^+$ concentration was increased from 318 to 360 mg·L^{-1} and Ca^{2+} concentration was decreased from 213 to 192 mg·L^{-1}. No significant increase in pH (from 7.50 to 7.62), Cl$^-$(from 286 to 299 mg·L^{-1}), NO_3^- (from 16.7 to 17.5 mg·L^{-1}), SO_4^{2-}(from 1025 to 1095 mg·L^{-1}) and PO_4^{3-}(<0.3 mg·L^{-1}) were observed using HWC. The applicability of the adsorbents in natural water is rarely studied in the literature. Malakootian et al. reported a decrease in fluoride concentration in Kuhbonan (Iran) water from 2.8 to 0.71 mg·L^{-1} at 20 g·L^{-1} of dose, 180 min and pH of the water by using a pumice, but they did not give any information about the final pH and the concentrations of mineral ions in water after defluoridation.[38]

5   Study limitation

Results obtained in this study illustrated that the heated washed clay seems appropriate for reducing fluoride in drinking water. The main limitation for its application to drinking water treatment is the relatively long period of time of adsorbent preparation.

6   Conclusion

Our findings show that the untreated natural clay chosen can reduce fluoride from water without any prior or subsequent adjustment of water pH. The BB model is fitted with a fluoride/natural clay adsorption system. The clay dosage has a determinant effect on the

removal efficiency while the contact time and the agitation speed are not significant. This prevents any significant interaction effects between these variables. However, a low level of contact time when the level of the agitation speed is high should be selected for reaching the maximal fluoride removal. The biopolymer-clay composites were unsuccessful in fluoride removal under the tested conditions. However, the thermally treated clays are very effective and a 97.5% reduction in dissolved fluoride could be reached. In natural water, the heated washed clay (HWC) can reduce F^- concentration to a permissible level without adjusting water pH before or after treatment. Large scale studies of the HWC adsorbent regeneration and adsorption experiments are suggested for future research.

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Conflict of interest

The authors have declared no conflict of interest.

References

1   Abtahi M, Dobaradaran S, Jorfi S, Koolivand A, Sadat Khaloo S, Spitz J, Saeedi H, Golchinpour N and Saeedi R, Age-sex specific disability-adjusted life years (DALYs) attributable to elevated levels of fluoride in drinking water: A national and subnational study in Iran, 2017. *Water Res* **157** : 94-105 (2019). DOI:10.1016/j.watres.2019.03.087

2   Chowdhury A, Adak MK, Mukherjee A, Dhak P, Khatun J and Dhak D, A critical revue on geochemical and geological aspects of fluoride belts , fluorosis and natural materials and other sources for alternatives to fluoride exposure. *J Hydrol* **574**: 333-359 (2019). DOI: 10.1016/j.jhydrol.2019.04.033

3   Bhaumik R, Mondal NK and Chattoraj S, An optimization study for defluoridation from synthetic fluoride solution using scale of Indian major carp Calta (Calta calta): An unconventional biosorbent. *J Fluor Chem* **195** : 57-69 (2017). DOI: 10.1016/j.jfluchem.2017.01.015

4   Guiza S, Brouers F and Bagane M, Fluoride removal from aqueous solution by montmorillonite clay: Kinetics and equilibrium modeling using new generalized fractal equation. *EnvironTechnol Innov* **21** : 101187 (2021). DOI: 10.1016/j.eti.2020.101187

5   Dobaradaran S, Ranjbar Vakil Abadi D, Mahvi AH and Javid A, Fluoride in skin and muscle of two commercial species of fish harvested off the Bushehr shores of the Persian Gulf. *Fluoride* **44** (3): 143-146 (2011).

6   Tangestani M, Mahvi MH, Dobaradaran S, Jamali M, Saeedi R and Spitzi J, Fluoride content and hazard quotient for beverages marketed in Iran. *Fluoride* **54** (2) : 178-192 (2021).

7   Dobaradaran S, Khorsand M, Hayati A, Moradzadeh R, Pouryousefi M and Ahmadi M, Data on fluoride contents in groundwater of Bushehr province, Iran. *Data Brief* **17** : 1158-1162 (2018). DOI: 10.1016/j.dib.2018.02.016

8   Karbasdehi VN, Dobaradaran S, Esmaili A, Mirahmadi R, Faraji Ghasemi F and Keshtkar M, Data on daily fluoride intake based on drinking water consumption

prepared by household desalinators working by reverse osmosis process. *Data Brief* **8** : 867-870 (2016). DOI: 10.1016/j.dib.2016.06.048

9   Hajiouni S, Dobaradaran S, Mahvi AH, Ramavandi B, Raeisi A and Spitzg J, Fluoride concentration in commercially available dairy milk in Iran. *Fluoride* **52**, no. 4 : 527-530 (2019).

10   World Health Organization, Guidelines for drinking-water quality: fourth edition incorporating the first addendum. https://apps.who.int/iris/handle/10665/254637 [accessed 09.11.2022]

11   Guissouma W, Hakami O, Al Rajab AJ and Tarhouni J, Risk assessment of fluoride exposure in drinking water of Tunisia. *Chemosphere* **177** : 102-108 (2017). DOI: 10.1016/j.chemosphere.2017.03.011

12   Kimambo V, Bhattacharya P, Mtalo F, Mtamba J and Ahmad A, Fluoride occurrence in groundwater systems at global scale and status of defluoridation. *Groundw Sustain Dev* **9** :100223 (2019). DOI: 10.1016/j.gsd.2019.100223

13   Ghanbarian M, Ghanbarian M, Mahvi AH and Tabatabaie T, Enhanced fluoride removal over $MgFe_2O_4$-chitosan-CaAl nanohybrid: Response surface optimization, kinetic and isotherm study. *Int J Biol Macromol* **148** : 574-590 (2020). DOI: 10.1016/j.ijbiomac.2020.01.143

14   Malakootian M, Fatehizadeh A and Yousefi N, Evaluating the effectiveness of modified pumice in fluoride removal from water. *Asian J Chem* **23** : 3691-3694 (2011).

15   Dobaradaran S, Kakuee M, Nabipour I, Pazira A, Zazouli MA, Keshtkar M and Khorsand M, Fluoride removal from aqueous solutions using Moringa oleifera seed ash as an environmental friendly and cheap biosorbent. *Fresenius Environ Bull* **24** : 1269-1274 (2015).

16   Dobaradaran S, Zazuli MA, Keshtkar M, Noshadib S, Khorsand M, Faraji Ghasemi F, Karbasdehi VN, Amiri L and Soleimani F, Biosorption of fluoride from aqueous phase onto Padina sanctae crucis algae: evaluation of biosorption kinetics and isotherms. *Desalin Water Treat* : 1-12 (2016). DOI: 10.1080/19443994.2016.1182081

17   Keshtkar M, Dobaradaran S, Nabipour I, Mahvi AH, Faraji Ghasemi F, Ahmadi Z and Heydaria M, Isotherm and kinetic studies on fluoride biosorption from aqueous solution by using cuttlebone obtained from the Persian Gulf. *Fluoride* **49** (3) : 343-351 (2016).

18   Malakootian M, Javdan M and Iranmanesh F, Fluoride removal study from aqueous solutions using Jajarm bauxite: Case study on Koohbanan water. *Fluoride* **48** (2) : 113-122 (2015).

19   Mobarak M, Selim AQ, Mohamed EA and Seliem MK, Modification of organic matter-rich clay by a solution of cationic surfactant/H_2O_2: A new product for fluoride adsorption fromsolutions. *J Cleaner Prod* **192** :712-721 (2018). DOI: 10.1016/j.jclepro.2018.05.044

20   Keshtkar M, Dobaradaran S, Keshmiri S, Ramavandi B, Arfaeinia H and Ghaedi H, Effective parameters, equilibrium, and kinetics of fluoride adsorption on *Prosopis cineraria* and *Syzygium cumini* leaves. *Environ Prog Sustainable Energy* **38** : S429-S440 (2019). DOI: 10.1002/ep.13118

21   Wang X, Pfeiffer H, Wei J, Dan J, Wang J and Zhang J, 3D porous Ca-modified Mg-Zr mixed metal oxide for fluoride adsorption. *Chem Eng J* **428** : 131371 (2022). DOI: 10.1016/j.cej.2021.131371

22   Bergaya F and Lagaly G, General Inroduction: Clays, clay minerals, and clay science, in Handbook of Clay Science, ed by Bergaya F, Theng B.K.G. and Lagaly G. *Elsevier*, The Netherlands, pp 1-18(2006).

23   Johnston CT, Clay mineral-water interactions, in Surface and interface chemistry of clay minerals, ed by Schoonheydt R, Johnston CT and Bergaya F. *Elsevier*, United States, pp 89-124 (2018). DOI: 10.1016/B978-0-08-102432-4.00004-4

24   Vinati A, Mahanty B and Behera SK, Clay and clay minerals for fluoride removal from water: A state-of-the artreview. *Appl Clay Sci* **114** : 340-348 (2015). DOI: 10.1016/j.clay.2015.06.013

25   Mourabet M, El Rhilassi A, El Boujaady H, Bennani-Ziatni M and Taitai A, Use of response surface methodology for optimizationof fluoride adsorption in an aqueous solution by Brushite. *Arab J Chem* **10** : S3292-S3302 (2017). DOI:

10.1016/j.arabjc.2013.12.028

26   Srasra E, Kebir-Ariguib N, Ayedi F, Bergaya F and Van Damme H, Mineralogical identification of bentonite claydeposit located near Gabes (Tunisia). *J Soc Chim Tunis* **II** : 37-45 (1988).

27   El Messabeb-Ouali A, Benna-Zayani M, M. Ayadi-Trabelsi M and Sauvé S, Morphology structure, thermal stability, XR-diffraction and infrared study of hexadecyltrimethylammonium bromide-modified smectite. *Int J Chem* **5** : 12-28 (2013). DOI: 10.5539/ijc.v5n2p12

28   Benna M, Kbir-Ariguib N, Magnin A and Bergaya F, Effect of pH on rheological properties of purified sodium bentonite suspensions. *J Colloid Interface Sci* **218** : 442-445 (1999). DOI: 10.1006/jcis.1999.6420

29   Darder M, Colilla M and Ruiz-Hitzky E, Chitosan-clay nanocomposites: application as electrochemical sensors. *Appl Clay Sci* **28** : 199-208 (2005). DOI: 10.1016/j.clay.2004.02.009

30   Abbassi H, Benna-Zayani M, Mezni M and Abidi R, Synthesis and chracterization of chloromethyl-calix[4]arene-grafted silylated clay nanocomposite. *J Nanopart Res* **23** :1-16 (2021). DOI: 10.1007/s11051-020-05135-8

31   Charbti M, Fortin C, Mezni M, Touati Hadjyoussef M and Benna Zayani M, Dealuminated heated clay as new fluoride adsorbent for treatment of contaminated drinking water. *C R Chim* **25** : 293-309 (2022). DOI: 10.5802/crchim.176

32   Goupy J and Creighton L, Introdution aux plans d'expériences, ed by Dunod, L'Usine Nouvelle. Paris, pp 1-324 (2006).

33   Natatou I, Marou G, Adamou Z, Moussa Y and Boos A, Cractérisation physico-chimique du gypse de Tahoua. *Int J Biol Chem Sci* **6** : 1324-13326 (2012). DOI: 10.4314/ijbcs.v6i3.35

34   Anbri Y, Tijani N, Coronas J, Mateo E, Menéndez M and Bentama J, Clay plane membranes : development and characterization. *Desalination* **221** : 419-424. DOI: 10.1016/j.desal.2007.01.101

35   Mourabet M, El Rhilassi A, El Boujaady H, Bennani-Ziatni M, El Hamri R and Taitai

A, Removal of fluoride from aqueous solution by adsorption on Apatitic tricalcium phosphate using Box-Behnken design and desirability function. *Appl Surf Sci* **258** : 4402-4410. DOI: 10.1016/j.apsusc.2011.12.125

36   Singh Solanki Y, Agarwal M, Gupta S, Shukla P, Maheshwari K and Midda MO, Application of synthesized Fe/Al/Ca based adsorbent for defluoridation of drinking water and its significant parameters otimization using response surface methodology. *J Environ Chem Eng* **7** : 103465 (2019). DOI: 10.1016/j.jece.2019.103465

37   Mahvi AH, Dobaradaran S, Saeedi R, Mohammadi MJ, Keshtkar M, Hosseini A, Moradi M and Faraji Ghasemi F, Determination of fluoride biosorption from aqueous solutions using *Ziziphus* leaf as an environmentally friendly cost effective biosorbent. Fluoride **51** (3) : 220 – 229 (2018).

38   Malakootian M, Moosazadeh M, Yousefi N and Fatehizadeh A, Fluoride removal from aqueous solution by pumice: case study on Kuhbonan water. *Afr J of Environ Sci Technol* **5** : 299-306 (2011).

39   Tangestani M, Naeimi B, Dobaradaran S, Keshtkar M, Salehpour P, Fouladi Z, Zareipour S and Sadeghzadeh F, Biosorption of fluoride from aqueous solutions by *Rhizopus oryzae*: Isotherm and kinetic evaluation. *Environ Prog Sustainable Energy* **41**: 1-10 (2021). DOI: 10.1002/ep.13725

40   Goswami A and Purkait MK, Kinetic and Equilibrium study for the fluoride adsorption using pyrophillite. *Sep Sci Technol* **46** : 1797–1807 (2011). DOI: 10.1080/01496395.2011.572327

41   Zhang Y, Xu Y, Cui H, Liu B, Gao X, Wand D and Liang P, La(III)-loaded bentonite chitosan beads for defluoridation from aqueous solution. *J Rare Earths* **32** : 458-466 (2014). DOI: 10.1016/S1002-0721(14)60094-6

42   Wolters F and Emmerich K, Thermal reactions of smectites-Relation of dehydroxylattion temperature to octahedral structure. *Thermochim Acta* **462** : 80-88 (2007). DOI: 10.1016/j.tca.2007.06.002

43   Rouahna N, Barkat D, Ouakouak A and Srasra E, Synthesis and characterization of Mg-Al layered double hydroxide intercalated with D2EHPA: Application for copper ions removal from aqueous solution. *J Environ Chem Eng* **6** : 1226-1232 (2018). DOI:

44   Malakootian M, Fatehizadeh A, Yousefi N, Ahmadian M and Moosazadeh M, Fluoride removal using Regenerated Spent Bleaching Earth (RSBE) from groundwater: Case study on Kuhbonan water. *Desalination* **277** : 244-249 (2011).

Figure captions

Figure 1   X-ray diffraction of the natural clay (HR), the purified clay (HP), the chitosan product (chitosan), the chitosan-purified clay composite (Chitosan-HP) and (3-Aminopropyl)trimethoxysilane-purified clay composite ($C_6H_{17}NO_3Si$ -HP).

Figure 2   X-ray diffraction of the purified clay (HP), the purified clay after heating (HHP), the purified clay using Na_2CO_3 (HP_0), the purified clay using Na_2CO_3 after heating (HHP_0), the washed clay (WC) and the washed clay after heating (HWC).

Figure 3   Normal probability plot.

Figure 4a   Response surface plot for clay dosage (X_1) – contact time (X_2) at fixed low level of agitation speed (X_3). Response: F%; X_1 = [0.5; 4 g/50 mL]; X_2 = [10; 1440 min]; X_3 = 60 rpm.

Figure 4b   Response surface plot for clay dosage (X_1) – contact time (X_2) at fixed center level of agitation speed (X_3). Response: F%; X_1 = [0.5; 4 g/50 mL]; X_2 = [10; 1440 min]; X_3 = 280 rpm.

Figure 4c   Response surface plot for clay dosage (X_1) – contact time (X_2) at fixed high level of agitation speed (X_3). Response: F%; X_1 = [0.5; 4 g/50 mL]; X_2 = [10; 1440 min]; X_3 = 500 rpm.

Figure 5   Conceptual mechanism of fluoride adsorption on heated washed clay.
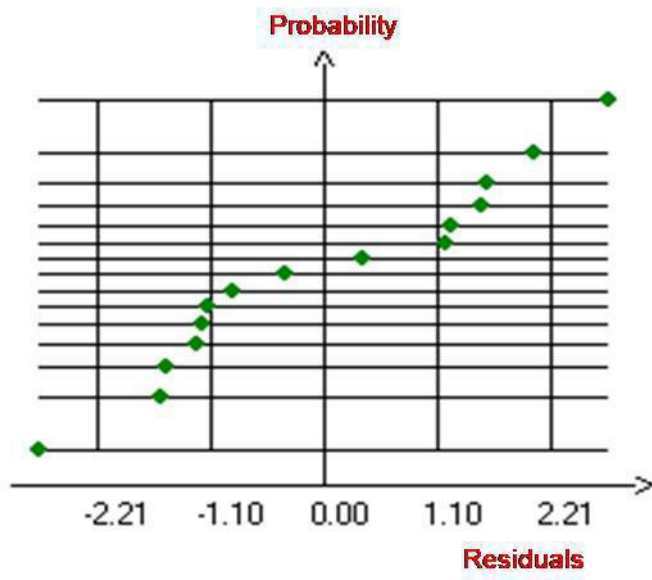
Table captions

Table 1   Box-Behnken design with the observed percent of the fluoride removal (F%). X_1, X_2 and X_3 are the clay dosage, the contact time and the agitation speed, respectively.

Table 2   Statistical significance of the Box-Behnken model coefficients.

Table 3   Analysis of variance (ANOVA) for fluoride/natural clay adsorption system through Box-Behnken model.

Table 4   Comparison between the developed adsorbents. F%: the observed percent of the fluoride removal; pH_f: Final pH of the water.

Table 5   Comparison between different fluoride adsorbents efficiencies in the literature.

Table 6   Physical-chemical analysis of the Tunisian drinking water before and after fluoride adsorption using heated washed clay (HWC) and heated purified clay using Na_2CO_3 (HHP_0).
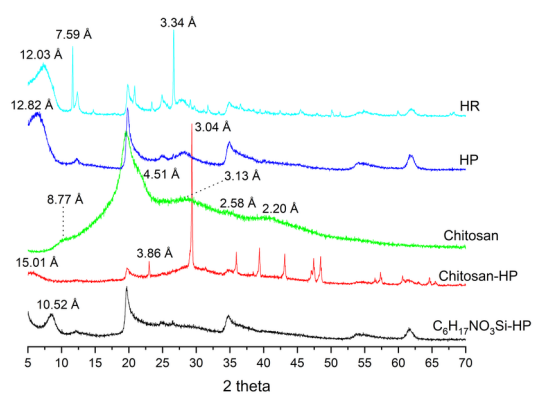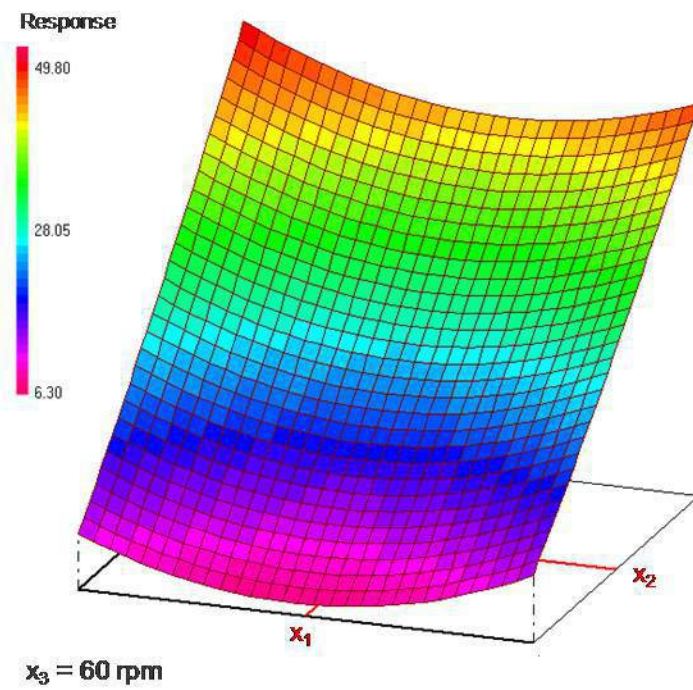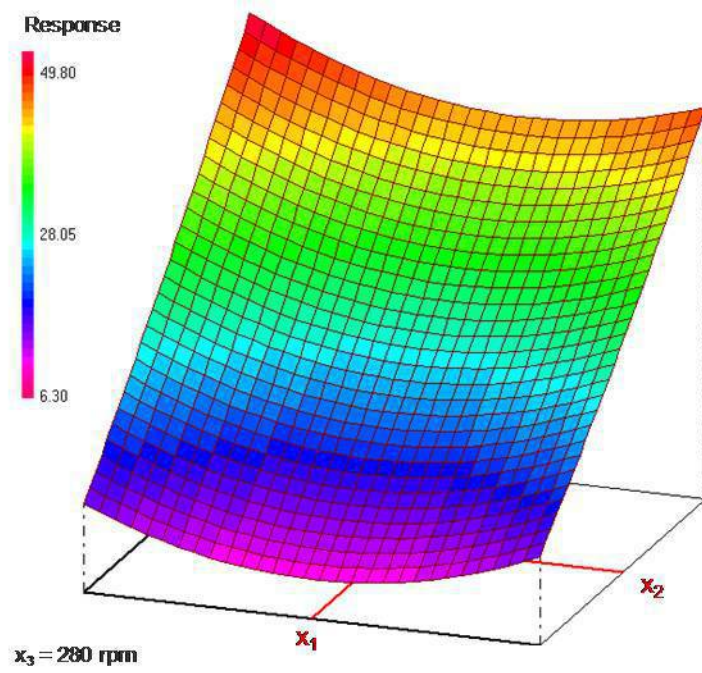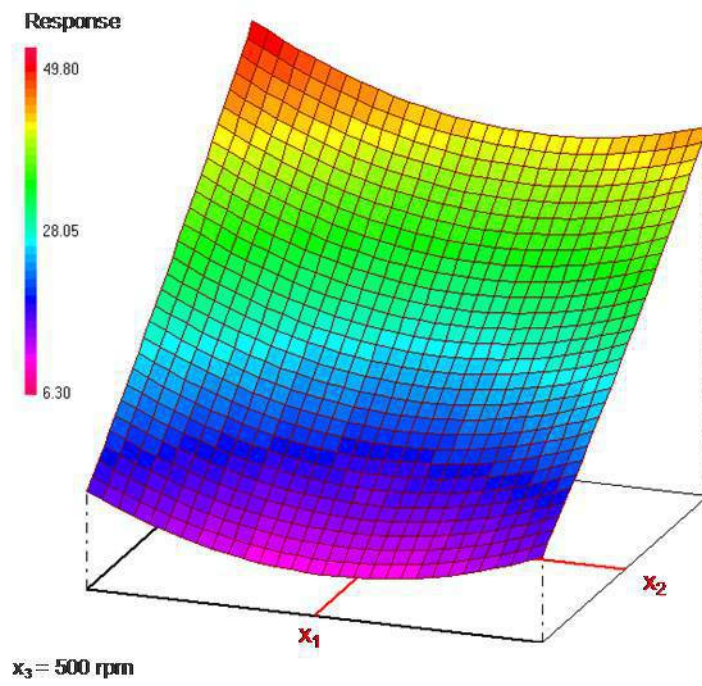
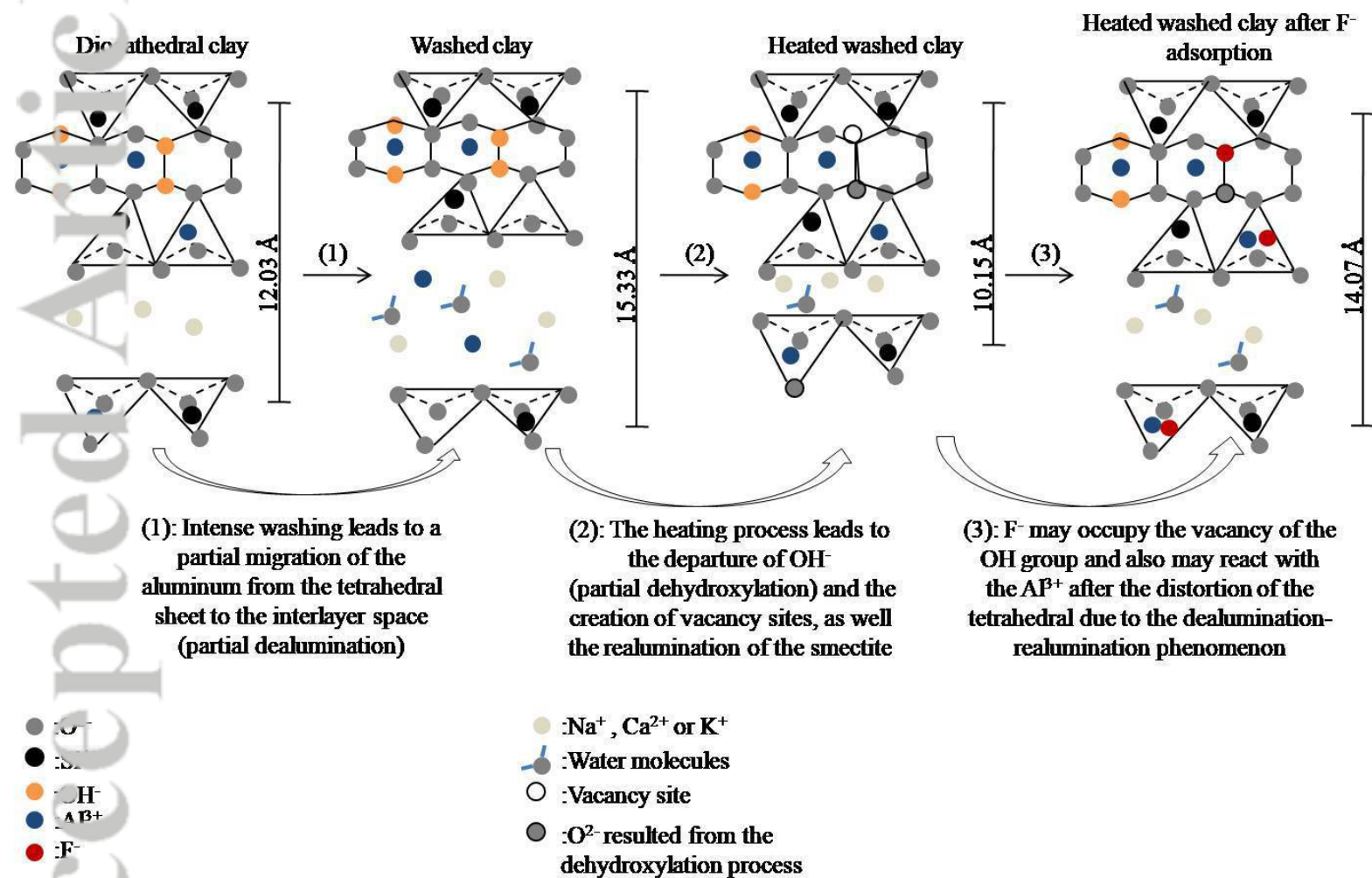JCTB_7336_Figure 1.tif
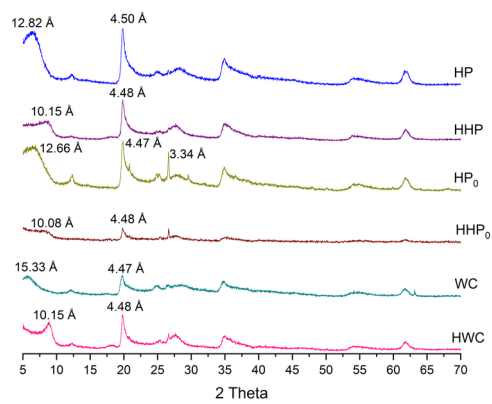
JCTB_7336_Figure 2.tif

JCTB_7336_Figure 3.jpg

JCTB_7336_Figure 4a.jpg

JCTB_7336_Figure 4b.jpg

Response

49.80

28.05

6.30

x_1

x_2

$x_3 = 500$ rpm

JCTB_7336_Figure 4c.jpg

Dioctahedral clay   Washed clay   Heated washed clay   Heated washed clay after F⁻ adsorption

12.03 Å   (1)   15.33 Å   (2)   10.15 Å   (3)   14.07 Å

(1): Intense washing leads to a partial migration of the aluminum from the tetrahedral sheet to the interlayer space (partial dealumination)

(2): The heating process leads to the departure of OH⁻ (partial dehydroxylation) and the creation of vacancy sites, as well the realumination of the smectite

(3): F⁻ may occupy the vacancy of the OH group and also may react with the Al^{3+} after the distortion of the tetrahedral due to the dealumination-realumination phenomenon

:O⁻
:Si
:OH⁻
:Al³⁺
:F⁻

:Na⁺ , Ca²⁺ or K⁺
:Water molecules
:Vacancy site
:O²⁻ resulted from the dehydroxylation process

JCTB_7336_Figure 5.jpg

Table 1

Experiment	X$_1$ (g·50 mL^{-1})		X$_2$ (min)		X$_3$ (rpm)		F (%)
	Coded	Experimental	Coded	Experimental	Coded	Experimental	
1	-1	0.5	-1	10	0	280	13.1
2	1	4	-1	10	0	280	50.5
3	-1	0.5	1	1440	0	280	13.1
4	1	4	1	1440	0	280	46.4
5	-1	0.5	0	725	-1	60	9.3
6	1	4	0	725	-1	60	41.9
7	-1	0.5	0	725	1	500	9.3
8	1	4	0	725	1	500	37.7
9	0	2.5	-1	10	-1	60	26.9
10	0	2.5	1	1440	-1	60	26.0
11	0	2.5	-1	10	1	500	32.4
12	0	2.5	1	1440	1	500	29.0
13	0	2.5	0	725	0	280	26.9
14	0	2.5	0	725	0	280	23.7
15	0	2.5	0	725	0	280	24.0

Table 2

Coefficient	Value	Standard deviation	t-Student	p-value
a_0	24.880	1.578	15.77	0.0001
a_1	16.450	0.966	17.03	<0.0001
a_2	-1.045	0.966	-1.08	0.333
a_3	0.527	0.966	0.55	0.612
a_{12}	-1.018	1.366	-0.74	0.494
a_{13}	-1.037	1.366	-0.76	0.486
a_{23}	-0.622	1.366	-0.46	0.669
a_1^2	0.929	1.422	0.65	0.547
a_2^2	4.959	1.422	3.49	0.0179
a_3^2	-1.276	1.422	-0.90	0.414

Table 3

Source	Sum of square	Degrees of freedom	Mean square	F-value	p-value
Model	2290	9	254	34.0	0.00124
Residual	37.3	5	7.47		
Lack of fit	31.1	3	10.4	3.30	0.241
Pure error	6.27	2	3.14		
Cor total	2330	14			

Table 4

Adsorbent	F%	pH_f
Chitosan-HP	0	6.83
$C_6H_{17}NO_3Si$-HP	6.5	9.79
Heated purified clay (HHP)	51.5	7.17
Heated washed clay (HWC)	89.7	6.16
Heated purified clay using Na_2CO_3(HHP$_0$)	97.5	5.58

	F%	pH_f

Table 5

Adsorbents	Dose (g·L^{-1})	time (min)	Initial F$^-$ concentration (mg·L^{-1})	F%	References
Cuttelbone	100	120	12	88.52	[17]
Pumice	20	180	2	85.75	[38]
0.3 M Hexadecyl trimethylammonium bromide modified pumice	20	180	2	94.75	[14]
Moringa oleifera ash	64	10	8	81.14	[15]
Rhizopus oryzae fungal biomass	2	30	2	90.05	[39]
Regenerated spent bleaching earth	20	240	2.5	74.01	[43]
Ziziphus leaf	10	90	12	100	[37]
Prosopis cineraria leaf	10	120	12	80.83	[20]
Syzygium cumini leaf	10	90	12	77.05	[20]
Jojarm bauxite	15	90	6	77.45	[18]
Padina sanctae crucis algae	48	5	8	97	[16]
Heated washed clay (HWC)	20	10	3.37	89.7	This study
Heated purified clay (HHP$_0$)	20	10	3.37	97.5	This study

Table 6

Parameters	Before adsorption	After adsorption	
		HWC	HHP$_0$
pH	7.50	7.62	7.64
F$^-$ (mg.L^{-1})	2.51	1.15	1.51
Cl$^-$ (mg.L^{-1})	286	299	322
NO$_3^-$ (mg.L^{-1})	16.7	17.5	17.6
SO$_4^{2-}$ (mg.L^{-1})	1025	1095	1158
PO$_4^{3-}$ (mg.L^{-1})	<0.3	<0.3	<0.3
Ca^{2+} (mg.L^{-1})	213	192	178
Mg^{2+} (mg.L^{-1})	101	72	74
Na$^+$ (mg.L^{-1})	318	360	413
K$^+$ (mg.L^{-1})	9.8	50.9	55.2