Original Research

A Comparison between Kaolin, Montmorillonite fe-Modified Montmorillonite as Candidate of Upflow Column Media Filter for Humic Acid Removal from SSAS

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Abstract

Humic acid (HA)-clay convoluted are well identified for their contribution to environmental processes. Upflow column filter experiments were performed in this study to scrutinize humic acid in simulated synthetic aqueous solution (SSAS) removal using kaolin, montmorillonite and fe-modified montmorillonite under different experimental conditions. The results showed that humic acid removal was higher in fe-modified montmorillonite clay than in kaolin and montmorillonite clays at optimum experimental conditions. The results show that the optimum removal efficiency of HA using femodified montmorillonite was 99 % for humic acid from simulated synthetic aqueous solution (SSAS) when pH = 1, flow rate = 15 ml/min, retention time = 90 min and initial HA concentration = 1 ppm. This efficiency was decreased with increasing of pH, flow rate and initial humic acid concentration while the removal efficiency increased with increasing retention time. This indicates that humic acid removal can be enhanced through the surface charge modification of montmorillonite, by replacing the natural interlayer cations of montmorillonite with polymeric Fe species, the properties of clay surfaces can be modified, and this allows them to interact with both organic and inorganic pollutants dissolved in water. The results of reusability of fe-modified montmorillonite clay obtained that only a slight loss in % HA removal efficiency was observed after five cycles of consecutive reusability, demonstrating that fe-modified montmorillonite was high-performance recyclable filter media for the removal of HA. Results of the experimental data show that the best empirical correlation achieved the most fitting of predicted % removal of HA from (SSAS) using fe-modified montmorillonite clay that gives the maximum value of ($R^2 = 0.9998$). Fe-modified montmorillonite is potential efficient filter media to be used as possible future promising development in filtration field.

Keywords: humic acid, kaolin, montmorillonite, modified montmorillonite

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Introduction

Natural raw water sources for the technological systems of water treatment plants contain numerous organic and inorganic constituents. The main group of natural organic matter (NOM) present in raw water sources are dissolved humic substances (HS). Humic substances are high molecular weight, complex, heterogeneous acidic polymers of yellow or brown colour [1]. They emerge in microbiological reactions resulting from the decomposition of dead plant and animal tissues. The composition of the resulting mixture is strongly dependent on the environmental conditions and the age of the material from which it was formed [2].

It is known that humic substances are very slowly biodegradable and are poorly soluble or insoluble in water. They are usually categorized by differences in solubility in aqueous solutions into humic acids, fulvic acids and humins. Humic acid (HA) is one of the major components of HS and generally presents as dissolved organic matter in water. It contains both hydrophobic and hydrophilic moieties as well as many organic functional groups such as carboxylic, phenolic, carbonyl, and hydroxyl groups connected with the aliphatic or aromatic carbons in the structure [3].

Humic acid is a primary target in water treatment processes even though they are not considered pollutants [4]. Negative effects of humic acid in drinkable water include undesirable color and taste, absorption and concentration of organic pollutants, as well as biochemical decomposition in water distribution systems. Humic acid also constitutes a potential source of energy and carbon for microbes dwelling in domestic and municipal water as well as in water pipes. Moreover, HA can act as a precursor for the formation of Disinfection By-Products (DBPs) during common chlorination of drinking water. Furthermore, HA can react with chlorine to form potentially carcinogenic chlorinated organic compounds [5].

Various approaches have been developed to remove humic acid from water, such as chemical coagulation, membrane separation, advanced oxidation, ion exchange, adsorption and filtration. Among them, filtration has been found to be superior to other techniques, particularly filtration using different types of clay in terms of initial cost, flexibility and simplicity of design, ease of operation, insensitivity to toxic pollutants, and reduced production of secondary harmful substances [4]. Recently, clays and its chemical modification represent a promising application in a variety fields for pollutants removal from aqueous solution due to their high surface area available for filtration, reactivity, time consuming and low-cost alternative operation. The chemical modification of different types of clays has been occurred by replacing the natural inorganic exchange cations with alkyl-ammonium, iron or sodium ions, clay surfaces are converted from being primarily hydrophilic to hydrophobic, which enable them to interact strongly

with organic vapors and organic contaminants dissolved in water, and the hydrophobicity of the modifiers (i.e., polymers) is the main factor controlling the filtration of organic pollutants with the modified clay [6].

The present study aims to optimize the performance of kaolin and montmorillonite as upflow column filter in the degradation efficiency of humic acid in simulated synthetic aqueous solution (SSAS) as well as develop a different method to enhance the removal of humic acid from (SSAS) using ferric modified montmorillonite clay (fe-modified mont.). Different experimental conditions as pH, flow rate, retention time and influent humic acid concentration have been examined to investigate their effects on humic acid removal efficiency and which combination would provide the optimum removal efficiency of HA. Once reliable data has been obtained from the first stage of experiments on (kaolin and montmorillonite) as filter media of upflow column filter system on the removal of HA in (SSAS), the results compared with ferric modified montmorillonite (fe-modified mont.) as filter media of upflow column filter to examine which type of filter media achieved the highest HA removal efficiency. This system was chosen because it is relatively economic, easy to set up and able to achieve high reactivity and reusability.

Materials and Methods

Study Area and Experimental Materials

This study has been conducted in Environmental Engineering Laboratory, Faculty of Engineering, Zagazig University. Commercial humic acid (CHA) was supplied by Sigma-Aldrich Chemicals Co., USA, in the form of the technical grade sodium humate is known to have an approximate molecular weight of 2000 g/mol. Commercial humic acid was used to make up the required concentrations of raw synthetic water for each of the model solutions. The kaolin and montmorillonite clays were bought from Industrial Zone - ElBasatin, Cairo, Egypt. The chemical composition of the used clays was determined in Table 1. Ferric oxide was used as surfactants to modify the utilized montmorillonite to produce (fe-modified mont.). Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Merck Chemical Co. All chemicals and reagents were analytical grade.

Preparation of Modified Montmorillonite Clay (fe-modified Mont.)

Cation exchange method was used to modify the montmorillonite by displacement of the sodium cations of montmorillonite with ferric oxide. Ferric oxide was introduced into raw montmorillonite clay with Cation Exchange Capacity, CEC 104.7 meq/100 g using a slightly modified method in [7]. Raw montmorillonite clay (10 g) was suspended in 55mL of deionized water

Chemical Com- position	SiO ₂	TiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃
% Weight of Kaolin	49.28%	0.06%	0.97%	35.69%	0.006%	0.07%	0.05%	0.28%	0.42%	0.12%	0.11%
% Weight of montmorillonite	69.8%	0.1%	1.0%	15.3%	0.009%	3.4%	1.9%	0.9%	0.9%	0.026%	0.04%
Physical properties, Particle size = 1.47 -1.68 mm.	рН	Porosity (%)	Particle density (g/cm ³)	Specific surface area (BET) (m²/g)	Cation exchange capacity (CEC), meq./100g		-	<u>`</u>			
% Weight of Kaolin	4 - 5	27	2-2.7	10.05±0.02	2.0 - 3.6	-					
% Weight of montmorillonite	2.8 - 3.8	17	1.2-2.6	83.79±0.22	104.7-110						

Table 1. The chemical composition for both of the used kaolin and montmorillonite clays.

at 600 rpm stirring. Na₂CO₃ (6.5 g) was dissolved in 50 mL of 0.2 M Fe (NO₃)₃ at constant stirring until homogenous mixture was formed. The mixture was aged for 26 hours. Then it was added drop wise to the clay suspension at stirring for two hours at 60°C. The sample was allowed to age for 20 h at room temperature, washed with deionized water, filtered, dried, and calcined on air at 300°C for 3 h.

Study Design, Column Experiment and Set up Establishments

Continuous comparative experimental model of study design has been carried out to determine the efficiency of kaolin and montmorillonite upflow filter media on the treatment of simulated synthetic aqueous solution contains humic acid effluent. Column experiments were performed at different conditions using a Plexiglas column (inner diameter 10 cm, outer diameter 14 cm, bed depth 50 cm). Stock solutions of humic acid were prepared by dissolving appropriate amounts of humic acid and covered with a porous plate of 5mm diameter pores (Sodium humate salt, Sigma-Aldrich Chemical Co., USA) in deionized water. Prior to the experiments, the packed column was flushed upward until the column effluents were clear and a steady state flow condition was established. In order to test the influence of different types of clays (kaolin and montmorillonite) on the removal efficiency of humic acid from simulated synthetic aqueous solution (SSAS) contains humic acid, two different packing orders of filter media were applied to the manufactured filter. After installation the filter media was filled in the filtration tank 5 cm depth with 10-15 mm grain size drainage layer at the bottom, 45 cm depth clay filter layer at the middle and distribution layer (1st run with kaolin clay and 2nd run with montmorillonite clay), (flat coarse gravel) was added 5cm depth at the top of the filter media to protect erosion of filter's top layer.

The experiments setup was divided into two stages. The 1st stage consisted of two runs with distribution layer (1st run with kaolin clay and 2nd run with montmorillonite



1st Stage (Kaolin & Montmorillonite) Clays Filter media unit

2nd Stage (Modified Montmorillonite) Clay Filter media unit

Fig. 1. Schematic layout for the components of the two stages of the upflow filter column all dimensions in (cm).

clay), for each run, the operating conditions were pH ranged from 1 to 5, flow rate ranged from 15 ml/min to 75 ml/min, treatment time ranged from 15 min to 90 min and initial feed concentration of humic acid ranged from 1 ppm to 50 ppm. The 2nd stage, the distribution layer of the 1st stage replaced with modified montmorillonite clay (fe-modified mont.) using the optimum conditions obtained from the 1st stage. Fig. 1. showed a schematic layout for the components of the two stages of the present study of the upflow filter column all dimensions in (cm). Then, humic acid solution was introduced upward to the packed column of the pump ranged (0.015-0.3) lit/min. The pump was Digital Watson Marlow model 505S. The pH of injected humic acid solution was adjusted using 1M HCl and/or 1M NaOH. Portions of the effluent were collected using the auto collector at a regular interval, and the concentrations of humic acid were determined at 254 nm using spectrophotometer (Spekol UV/VIS).

Measurements and Analysis

The physicochemical analysis of simulated synthetic aqueous solution of humic acid samples has been done using standard methods. In the 1st stage of this study, first, optimum operating pH was determined for maximum removal of humic acid by running the experiment for 1, 2, 3, 4 and 5. Second, at the optimum pH, optimum flow rate was determined for maximum removal of humic acid by running the experiment for 15, 25, 35, 45, 60 and 75 ml/min, respectively. Third, at the optimum pH and flow rate, the retention time was determined for maximum removal of humic acid by running the experiment for 15, 30, 45, 60, 75 and 90 min respectively. Finally, at the optimum pH, flow rate and retention time, optimum initial feed concentrations of humic acid were determined for maximum removal of humic acid by running the experiment for 1, 10, 20, 30, 40 and 50 ppm, respectively.

All the previous steps repeated for $(1^{st}$ run with kaolin clay and 2^{nd} run with montmorillonite clay) upflow filter media. The optimum conditions achieved from the 1^{st} stage repeated for ferric modified montmorillonite clay (fe-modified mont.) upflow filter media which represented the 2^{nd} stage of the study.

Filtrated Sample was taken by 1 liter plastic bottle after each fixed retention time and the analytical parameter was humic acid concentration. Table (2) shows set of stages performed for upflow filter media with different clay units at several boundary conditions.

pH were measured by AD1000 (pH/mv) & temperature meter. In order to avoid interference with other elements in wastewater, the experiments in this study were carried out using simulated synthetic aqueous solution (SSAS) of different humic acid. 1000 mg/l stock solution of humic acid was prepared by dissolving known weight of humic acid in one liter of double distilled water, all solutions using in the experiments were prepared by diluting the stock solution with double distilled water to the desired concentrations for the experimental work of this investigation. Determination of humic acid concentration in simulated synthetic aqueous solution (SSAS) contains humic acid samples and standard concentrations of humic acid were done according to APHA (2005) using spectrophotometer (Spekol UV/VIS) at wavelength 254 nm. A standard line was prepared by plotting the absorbance reading on Y-axis versus the concentration of each standard solution of humic acid on X-axis Fig. 2.

Reusability of Modified Montmorillonite Clay

In order to check the reusability of the upflow filter media represented in ferric modified montmorillonite clay (fe-modified mont), which was filtered, washed with distilled water, and dried in the oven at 100°C for 12 h followed by calcination at 300°C for 4 h to remove any occluded material before reuse. To evaluate the reusability of the ferric modified montmorillonite clay, removal of HA and regeneration of HA-loaded through clay voids was performed in five consecutive cycles. In each cycle, initial concentration of HA = 1 ppm, pH = 1, flow rate = 15 L/min and retention time = 90 min which are the conditions of experiment gives the optimum percent removal of humic acid from SSAS aforementioned. The destined percent removal and number of repeated uses were dependent on humic acid; thus five times of use of upflow filter media unit was seen to be feasible.

Table 2. Set of stages performed for upflow filter media with different clay units at several boundary conditions.

	1 st	2nd Stars		
Boundary Conditions	Run (1)	Run (2)	2 Stage	
	Kaolin clay filter media unit	Montmorillonite clay filter media unit	Modified montmorillo- nite clay filter media unit	
рН	1, 2, 3, 4, 5	1, 2, 3, 4, 5	1	
Flow rate (ml/min)	15, 25, 35, 45, 60, 75	15, 25, 35, 45, 60, 75	15	
Retention time (min)	15, 30, 45, 60, 75, 90	15, 30, 45, 60, 75, 90	90	
Initial feed conc. Of HA (ppm)	1, 10, 20, 30, 40, 50	1, 10, 20, 30, 40, 50	1	



Fig. 2. Calibration curve of humin acid concentration.

Data Quality Management

To declare quality of the data by minimizing the errors the following measures had been undertaken: Apparatuses were calibrated; expiry date of reagents had been checked before starting the real analysis and standard control also prepared. Each test had triplicated.

Statistical Analysis

All experimental data of this study used to correlate the relationship between dependent and independent variables affecting on the removal efficiency of humic acid using kaolin, montmorillonite and ferric modified montorillonite clays through regression analysis carried out with the help of Excel Software 2016. In this study, there is one dependent variable (% removal of humic acid) based on four independent variables (pH, flow rate, retention time, diameter of filter column and initial feed concentration of humic acid).

Results and Discussion

The ability of different kinds of clay represented in kaolin, montmorillonite and ferric modified montmorillonite (fe-modified mont.) to remove humic acid from SSAS in fixed bed column of continuous mode at various boundary conditions which are pH's of SSAS of humic acid (pH), flow rates of SSAS (Q), Retention time of treatment (t) and initial concentration's of SSAS of humic acid (C_0) was investigated. Thus, the results obtained are explained below.

Influence of pH on the Removal of HA from SSAS

The results showed that using kaolin, montmorillonite and ferric modified montmorillonite (fe-modified mont.) clays, the percent removal of humic acid was increased when the pH of SSAS of humic acid was decreased at constant other boundary conditions as shown in Fig. 3. The optimized pH for humic acid removal efficiency by kaolin, montmorillonite and ferric modified montmorillonite (fe-modified mont.) media



Fig. 3. % HA removal efficiency based on pH using different types of clays of filter media at init. conc. = 50 ppm, flow rate = 15 L/min and R.T = 15 min.

filters separately were found to be 1.0 with 65%, 70% and 81% removal efficiency respectively.

This increase can be explained as follows: humic acid is predominately negatively charged. Therefore, decreasing the pH renders the negatively charged humic acid molecules more neutral. A negatively charged molecule attracts ions of opposite charge (hydrogen ions in this case) to its surface from the surrounding water and becomes more neutral. A neutral molecule is inherently less soluble in water than a charged molecule (water is highly polar solvent) and, therefore, more adsorbable. In addition, at low SSAS pH, humic acid is more coiled due to less negative-charge repulsion allowing for greater access to kaolin, montmorillonite and modified montmorillonite pores. The results showed that ferric modified montmorillonite (fe-modified mont.) clay achieved the highest HA removal efficiency that refers to the electrostatic attraction between surfaces positive charge (Fe-modified mont.) and surface negative charge of HA increases, hence removal of HA increases. In other words, the filtration process become more favorable as SSAS pH decreased [8]. The result of the present study is consistent with the results of [9] who have reported that the % removal of humic acid decreased with increasing pH from 2.5 to 7.5. Also, the result agreed with the results of [10, 11].

Influence of Flow Rate on the Removal of HA from SSAS

The results illustrated that when the flow rate of SSAS of humic acid was increased, the percent removal of humic acid was decreased at constant other boundary conditions as shown in Fig. 4. The results obtained that the highest removal efficiency of HA achieved at flow rate 15 ml/min was 65%, 70% and 81% for kaolin, montmorillonite and ferric modified montmorillonite (fe-modified mont.) clays respectively.

This may be due to the fact that when the flow of SSAS of humic acid increasing, the velocity of solution in the column packed with kaolin, montmorillonite and ferric modified montmorillonite (fe-modified mont.) clays separately was increasing too, so the solution spend shorter time than that spend in the column while



Fig. 4. % HA removal efficiency based on flow rate using different types of clays of filter media at init. conc. = 50 ppm, Ph = 1 and R.T = 15 min.

at low flow rate, the SSAS of humic acid resides in the column for longer time, and therefore undergoes more treatment with filter media, thus the different types of clays of filter media uptake low amount of humic acid from SSAS of humic acid for high flow rate, therefore the percent removal of humic acid was decreased when the flow rate was increased. This consequence agreed with [12] regard to the removal of humic acid from aqueous solutions using rice husk.

Influence of Retention Time on the Removal of HA from SSAS

The results demonstrated that when the retention time of SSAS of humic acid increased the percent removal of humic acid increased at constant other boundary conditions as shown in Fig. 5. The optimized retention time for humic acid removal efficiency by kaolin, montmorillonite and ferric modified montmorillonite (fe-modified mont.) media filters separately were found to be 90 min with 80%, 88% and 94% removal efficiency respectively.

This may be due to the fact that when the time of treatment of SSAS of humic acid increasing and the velocity of SSAS in the column packed with different filter media clays was remaining constant, the solution spend longer time than that spend it when the time of treatment decreased, so the filter media uptake more amount of humic acid from SSAS, therefore the percent



Fig. 5. % HA removal efficiency based on retention time using different types of clays of filter media at init. conc. = 50 ppm, flow rate = 15 L/min and pH = 1.

removal of humic acid from SSAS was increased. Comparable outcomes with regard to the removal of humic acid, by using different types of clay media filters were reported by various researchers [13-18].

Influence of Initial Concentration of HA on the Removal of HA from SSAS

The results showed that the percent removal of humic acid was decreased when the initial concentration (C_o) of SSAS of humic acid was increased at constant other boundary conditions as shown in Fig. 6.

This can be explained by the fact that the initial concentration of humic acid had a restricted effect on humic acid removal capacity; simultaneously the different types of used clays of filter media had a limited number of active sites, which would have become saturated at a certain concentration. This was lead to the increase in the number of humic acid molecules competing for the available functions groups on the surface and void ratios of filter media. Since the solution of lower concentration has a small amount of humic acid than the solution of higher concentration of it, so the percent removal was decreased with increasing initial concentration of humic acid. For kaolin, montmorillonite and ferric modified montmorillonite (fe-modified mont.) clays, higher percent removal were 88%, 93% and 99% respectively for humic acid at initial humic acid concentration of 1 mg/l, so ferric modified montmorillonite was found to be the most efficient to humic acid removal from SSAS and wastewater. This result agreed with [19, 20].

Reusability and Regeneration Studies

The economic efficiency and environmental sustainability should be taken into account during the process of wastewater treatment. Reusability and regeneration studies will help to elucidate the nature of filtration process and to reuse the filter media. Fig. 7 shows the result of five reusability studies on the fe-modified montmorillonite clay as filter media for the removal of HA from SSAS with 99, 98.4, 97.7, 97.3, 97.2, 97.2 % after 1st, 2nd, 3rd, 4th, 5th and 6th reuse,



Fig. 6. % HA removal efficiency based on initial conc. using different types of clays of filter media at flow rate = 15 L/min, pH = 1 and R.T = 90 min.



Fig. 7. % HA removal efficiency using fe-modified montmorillonite clay as filter media with six reusability-regeneration cycles. (filtration conditions: pH = 8.0, flow rate = 15 L/min, R.T = 90 min and initial HA concentration = 1 ppm).

respectively, during a 90 min study. The capacity of the ferric modified montmorillonite clay upflow filter media was found to be decreased until be constant at destined percent removal after five times repeated use. Only a slight loss in % HA removal efficiency was observed after five cycles of consecutive reusability, demonstrating that fe-modified montmorillonite was high-performance recyclable filter media for the removal of HA.

The higher reusability of the fe-modified montmorillonite can be ascribed to its preparation protocol, especially the careful selection of calcination conditions. In addition, the ability of the fe-modified montmorillonite clay to provide sufficient anchor for the Fe ion on the extended surface area of monorillonite clay which is a promising support for industrial application. This result agreed with [16].

Statistical Model

A statistical model was carried out on the experimental results obtained from this study. Regression Analysis was adopted to maintain a relation between the percent removal of humic acid and pH of feed solution, the flow rate, retention time, initial concentration of humic acid and filter diameter. Fig. 8 shows a plot of the predicted % removal of HA using fe-modified montmorillonite clay comparing to the



Fig. 8. Correlation between experimental and predicted % HA removal using fe-modified montmorillonite clay as filter media.

experimental data results. This relation is shown in Equation (1) below, which has a correlation coefficient (R^2) 0.9998 which means all values of % removal of HA using fe-modified montmorillonite clay as filter media obtained from the empirical correlation are very close to values determined experimentally.

% R = -3.438 pH - 0.302 Q + 0.175 t
- 0.069 C₀ + 9.011
$$\Phi$$
 (1)

...where % R is Percent Removal of Humic Acid from SSAS, Q is aqueous solution flow rate, (L/min), C_o is initial concentration of Humic Acid, (ppm), t is retention time, (min) and Φ is internal diameter of filter column, (cm).

From the experimental data, by applying linear equation regression model with confidence level 95% to correlate, predict and understand which among the independent variables (pH, Q, t, C_0 and Φ) are related to the dependent variable (% Removal of Humic Acid from SSAS), and to explore the forms of this relationship. After several trials to minimize the residual mean square (RMS) and achieve the highest, value of R². Results of the experimental data show that the best empirical correlation achieved the best fitting of predicted % removal of HA using fe-modified montmorillonite clay that gives the highest value of $(R^2 = 0.9998)$ which can be expressed as Eq. (1). The results of regression model indicate that the most influential independent variables in the % removal efficiency of HA from SSAS using fe-modified montmorillonite clay upflow filter retention time and internal diameter of filter column, which affects positively. The least influential independent variables are pH, flow rate and the initial concentration of HA, which affects negatively as can be seen in the Eq. (1).

Conclusions

Upflow column filter experiments were performed to scrutinize humic acid in simulated synthetic aqueous solution (SSAS) removal using kaolin, montmorillonite and fe-modified montmorillonite) under different experimental conditions allowed for the following conclusions to be made:

- Results showed that humic acid removal was higher in fe-modified montmorillonite clay than in kaolin and montmorillonite clays at optimum experimental conditions.
- Results show that the optimum removal efficiency of HA using kaolin, montmorillonite and fe-modified montmorillonite were 88%, 93% and 99 % respectively for humic acid from simulated synthetic aqueous solution (SSAS) when pH = 1, flow rate = 15 ml/min, retention time = 90 min and initial HA concentration = 1 ppm.
- The results indicate that humic acid removal can be enhanced through the surface charge modification

of montmorillonite. The removal of humic acid in kaolin, montmorillonite and fe-modified montmorillonite was influenced by pH, flow rate, retention time and initial humic acid concentration.

- Also, the removal efficiency of humic acid in simulated synthetic aqueous solution (SSAS) removal using kaolin, montmorillonite and femodified montmorillonite was decreased with increasing of pH, flow rate and initial humic acid concentration while the removal efficiency increased with increasing retention time.
- The results of reusability of fe-modified montmorillonite clay obtained that only a slight loss in % HA removal efficiency was observed after five cycles of consecutive reusability, demonstrating that fe-modified montmorillonite was highperformance recyclable filter media for the removal of HA.
- Results of the experimental data show that the best empirical correlation achieved the most fitting of predicted % removal of HA from (SSAS) using fe-modified montmorillonite clay that gives the maximum value of ($R^2 = 0.9998$).

Finally, the present findings highlighted that fe-modified montmorillonite possessed great potential efficient filter media to be used as possible future promising development for effective removal of HA from aqueous solutions and in filtration field.

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Conflict of Interests

The author declare no conflict of interests.

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