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Removal Of Total Nitrogen And Phosphorus Present In Fish Ponds Wastewater By Calcined Diatomite

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Abstract:*This work aims to enhance and improve the quality of a thermally modified diatomite from the Algerian Sahara through various physicochemical methods. The BET analysis reveals that calcining the diatomite at 850°C increased its specific surface area. Diffractograms and infrared spectra reveal new phases and surface function, confirming the surface modification that increased the zero-charge point. The* PH_{PZC} *value for calcined diatomite is 8.8 while the raw diatomite's is 7.8. We conducted a mode study on the dynamic adsorption of chemical pollutants like total nitrogen and phosphates to simulate the impact of modifications on adsorption. We achieved an adsorption rate of 90% for pollutants treated on diatomite. The results obtained show the success of the test for all treated pollutants. The use of calcined diatomite in the treatment and filtration of polluted water has demonstrated the effectiveness of this material in eliminating and improving the quality of filtered water.*

Keywords: *Diatomite, characterization, thermal treatment, wastewater treatment, total nitrogen, phosphate, Ougarta*

INTRODUCTION

Mostly made of amorphous silica (SiO_2), diatomite finds widespread use in the filter aids industry, environmental pollution remediation, and functional materials because of its special physical and chemical characteristics [1].

The permeability and whiteness of diatomite filter aids are improved by a very important process, which is Flux calcination. Despite the abundance of diatomite resources on earth, the raw diatomite contains various impurities that reduce the content of useful SiO2 and porosity [2].The majority of research concentrates on the adsorption properties of diatomite. The origin of diatomite heavily influences its application in wastewater treatment, necessitating further efforts to enhance its adsorption capacity [3].

This study aims to characterize the physicochemical and textural properties of raw and modified diatomite from the Algerian Sahara and evaluate its application in the removal of phosphorus and total nitrogen present in fish pond wastewater.

MATERIALS AND METHODS

Area study

This work collects the natural diatomite. The study area is located in the Western Sahara of Algeria. This region lies to the west of Erg Er Raoui (Fig. 01). This region is of enormous significance in the Western Sahara for the study of lacustrine phases associated with the Holocene humid maximum. The study sector is part of a lacustrine system that we refer to in this work as the "Hassi Manda Lacustrine System." (Fig.1) [4,5].

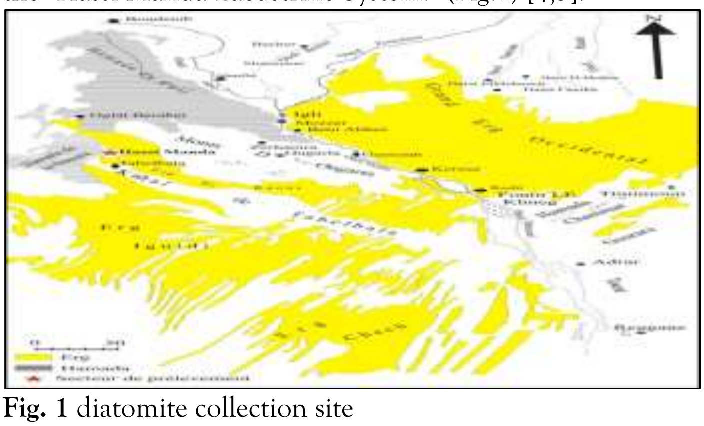

Fig. 1 diatomite collection site

Sample wastewater

The aquaculture research center collects wastewater samples from its fish farm ponds. It specializes in breeding tilapia and aims to produce 50 tons of fish. It is located in Boukais in the province of Bechar in the southwest of Algeria, between Latitude: 31.5° N and Longitude: 2.6° West [6].

METHODS

We thermally treated raw diatomite at 850 °C in a muffle furnace. We used X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and BET to look at the structure and microstructure of a natural and calcined diatomite from southwest Algeria. We determined physical properties such as porosity and apparent density using a porosimeter and European standards EN-1936 (2006) [7].

In the Bechar region of southwest Algeria, a polluted aquaculture pond effluent meant for untreated irrigation was filtered for phosphates and total nitrogen using calcined diatomite powder at 850°C. Dynamic adsorption in fixed beds was conducted in glass mini-columns employing the method of ROSENE and MÂNES [8].

We observed the impact of altering the experimental parameters, like the height of the adsorbent bed, while maintaining a steady flow rate. We determined the phosphate and total azote content of the raw and filtered water using the standard methods cited by Rodier et al. 2009 [9].

The experimental data were correlated with the two mathematical models Bohart & Adams and Wolborska.

BOHART- ADAMS model (1920) [10]

$$\boldsymbol{ln\frac{C_e}{C_0} = KC_0 t - KN_0\frac{z}{U}}$$

With:

K : is the adsorbate-adsorbent adsorption kinetic constant in m3.kg-1.min-1

N0: is the maximum volumetric adsorption capacity in kg.m-3

Ce : equilibrium solute concentration kg.m-3

C0: initial concentration of solute in solution kg.m-3

U : migration speed m.min-1

Z : adsorbent bed height m.

WOLBORSKA model (1989) [11]:

$$\mathbf{Ln}\frac{C_e}{C_0} = \frac{\beta_a C_0}{N_0}t - \frac{\beta_a Z}{U} \qquad \text{avec} \qquad V = \frac{U.C_0}{N_0+C_0}$$

With:

βa : Kinetic coefficient of mass transfer.

U : Filtration speed (m/h)

C_0 : Initial solute concentration (mg/l)

N_0 : Maximum adsorption capacity (mg/g)

V : adsorption front speed in (m/h)

RESULTS

Natural and calcined diatomite characterization results

Some methods used to describe the material, like, X-ray diffraction, scanning electron microscopy, Fourier transform infrared, nitrogen absorption by BET, and finding out the density and porosity percentage, led to the following findings (Table 1).

There is a wide variety of shapes found in natural diatomite, especially the circular, rod-like formations called piquants and centrosomes. The surface consists of many components, including silica (SiO_2) (81.66), alumina (Al_2O_3), and calcium carbonate ($CaCO_3$).

These materials occupy the pores within the diatomite, resulting in decreased porosity and increased density.

At temperatures of 850 °C, diatomite experiences notable structural and textural changes. A substantial percentage increase in porosity from 35 to 70% results from the removal of different

water molecules, organic matter, and carbonates, which results in a loss of mass, and particle coalescence, which causes structural rearrangement and densification (Table 1).
Upon heating, new vibrational bands of cristobalite and surface silanol groups emerge. The carbonate bands disappear, and diatomite ceases to contain any hydroxyl groups. This renders the material more porous and decreases its density by a specific proportion.

Table 1: Major chemical compositions, porosity percentage, and apparent density of raw and calcined diatomite

Physicochemical properties	SiO2(%)	CaO3(%)	Al2O3(%)	Apparent density [g/cm]	Total porosity [%]
Natural diatomite (DN)	81,66	13	5,140	0,92	35
DN at Temperature 850°C	88.13	6,5	0,410	0,55	70

Results of wastewater treatment by calcined diatomite

The physicochemical studies of the contaminated water indicate phosphate and total nitrogen contents of 3.2 mg/l and 40 mg/l, respectively. These values surpass Algerian requirements.
We evaluated the adsorption or retention capacity of diatomite by tracking the evolution of the fraction (C_e/C_0) of each parameter as a function of filtration time. This fraction plots the ratio of the filtrate's pollutant content at the column outlet to its initial presence in the aquaculture effluent over time, allowing for the plotting of the breakthrough curve. We calculate the breakthrough time, also known as the filter breakdown time, from the breakthrough curve to ascertain the validity of the purification process, which aligns with the efficiency of the calcined diatomite fixed bed.
Figures 2 and 3 display the revolution curves obtained at different heights (2 and 3 cm) of the diatomite bed and a flow rate Q = 2.5 ml/min; the results show that increasing the bed height from 2 to 3 cm increases the breakthrough time from 12 to 25 h and the effluent volume from 650 to 950 ml (Fig. 1).
Calcined diatomite pollutes water, removing 80% and 92% of the total nitrogen and phosphate ions, respectively. The results of diatomite zero-point pH determination indicate that its pH_{PZC} is 8. At pH levels below the point of zero charge (PZC), the surface of the material possesses a positive charge; conversely, at elevated pH levels, it exhibits a negative charge [12, 13].The wastewater pH (6.5) is below the isoelectric point, resulting in a positively charged surface of the diatomic adsorbent, which enhances the adsorption of total nitrogen and phosphate ions.

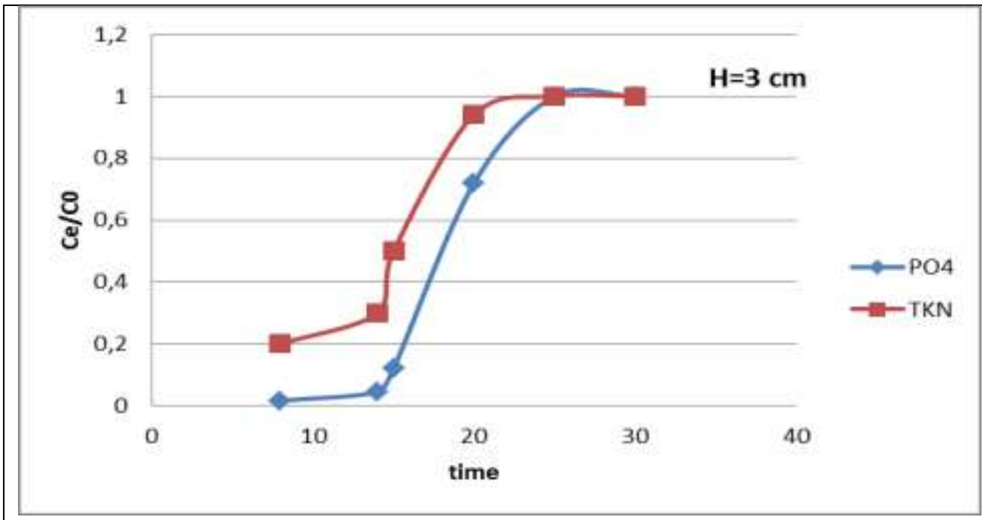

Fig. 2. Breakthrough curve for PO_4 and NTK from wastewater at bed height of 3 cm and a constant flow rate of 2 mL/(min)

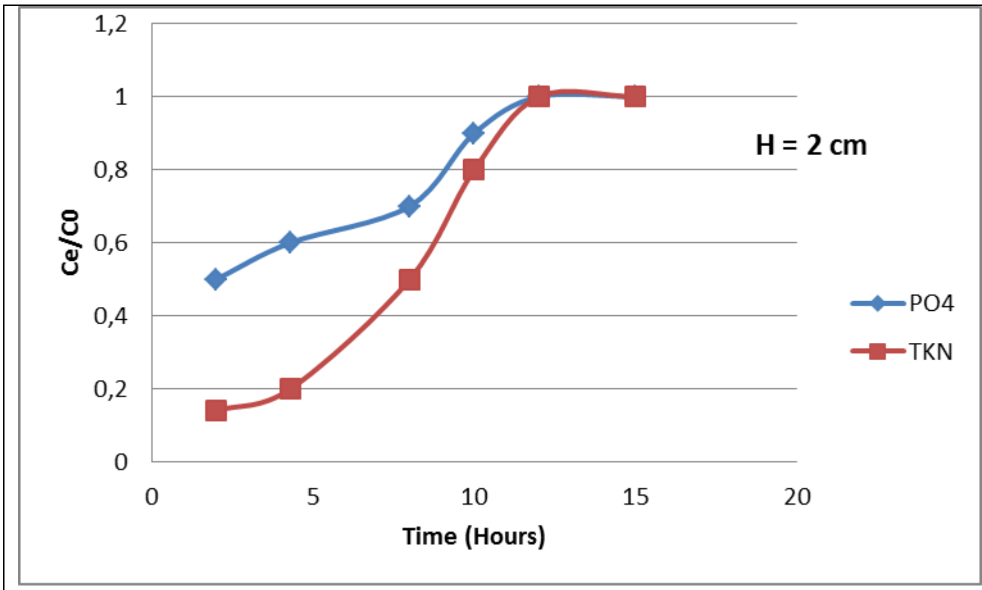

Fig. 3. Breakthrough curve for PO_4 and NTK from wastewater at bed height of 2 cm and a constant flow rate of 2 mL/(min)

The tables 2and 3 display the modeling results. From these results, we can see that the experimental results obey the BOHART-ADAMS model, with correlation coefficients over 0.9 for the two different adsorbent bed heights used. We discovered that the height of the adsorbent bed influences the rate constant. Furthermore, the rate constant increases with decreasing bed height. As the adsorbent bed height increases, the quantity adsorbed rises, yet it consistently reaches the adsorption limit. The best results observed are for a height of 3 cm.

Table 2: BOHART & ADAMS models results

Physicochemical Parameters	BOHART and ADAMS model		
	Parameters	H = 2 cm	H= 3 cm
PO_4^{-3}	K (l/mg.h)	0.07677273	0.41113636
	N_0 (kg.m^3) Equation Correlation coefficient	0.04848493 y= 0.168x-0.809 R^2= 0.931	0.4282399 y= 0.904x-15.31 R^2= 0.909
TKN	K (l/mg.h)	0.01607143	0.1075714
	N_0 (kg.m^3)	0.69574898	0.66888765
	Equation Correlation coefficient	y= 0.562x-2.430 R^2= 0.988	y= 0.376x-6.252 R^2= 0.925

Table 3: WOLBORSKA models results

Paramètre physicochimique	WOLBORSKA model		
	Parameters	H = 2	H =3
PO_4^{-3}	βa (h^{-1})	0,10666684	0,0176065
	N_0 (mg/g)	1,3893845	0,04282399

	U (m/s)	0,0046	0,0023
NK	**β**a (h^{-1})	0,01118168	0,00719532
	N_0 (mg/g)	0,69574898	0,66888765
	U (cm/s)	0,0046	0,0023

DISCUSSION

Diatomite, also known as diatomaceous earth, mostly comprises amorphous silica (SiO_2) originating from the remains of diatom shells. Diatomite, as a non-metallic mineral raw material, exhibits remarkable effectiveness in the filter aids industry and environmental remediation owing to its beneficial chemical and physical properties, such as acid resistance, large surface area, and high adsorption capacity [14, 15, 16].

Mineralogical analyses conducted on the diatomite utilized in this investigation indicated the presence of carbonates. These ions can sequester hydroxyl radicals, resulting in the formation of carbonate radicals, which exhibit lower reactivity than hydroxyl radicals. Although diatomite resources are plentiful on Earth, raw diatomite is laden with various contaminants, including carbonates, iron oxide, and organic matter, which diminishes the beneficial SiO_2 concentration. The existence of contaminants inevitably constrains the economic and environmental uses of diatomite. [17], [18], [19].

Thermal treatment of raw diatomite, by removing organic materials from $CaCO_3$ and ferric hydroxides (Fe2O3), eradicates nanofacies and alters specific sediment properties, leading to a mineralogical transformation by water loss into opal (SiO_2, n H2O), which subsequently converts into cristobalite. Khraisheh and colleagues have previously documented this phenomenon at a temperature of 980 °C [20, 21].

In industrial contexts, calcination and flux calcination at elevated temperatures (above 800 °C) are established methods for eliminating organic matter and partially removing metallic oxides from raw diatomite, while simultaneously enhancing its porous structure. The whiteness of calcined diatomite can also be notably improved, and its permeability properties are enhanced post-calcination [22]. However, during this process, the porous structure of diatomite may be compromised, resulting in the loss of silanol groups (Si-OH) from its surface. This significantly reduces the absorption capacity of diatomite [23].

We achieved dynamic adsorption of TKN and phosphate ions on a calcined diatomite fixed bed at a lower flow rate. In this instance, these ions had more time to come into contact with the adsorbent, resulting in greater removal of these ions from the fixed-bed column. These results are in agreement with those reported in previous studies [24].

Revolution curves show that adsorption happens very quickly. This is likely because there are lots of places around or inside the diatomite particles where ions can be captured. Heightening the bed lengthens the breakthrough time and increases the effluent volume. Increasing diatomite mass may provide more adsorption sites, explaining this phenomenon [25]. The slope of the breakthrough curve decreased with increasing bed depth, leading to a widening of the mass transfer zone [26, 27].

We use the Bohart-Adams and Wolborska models to determine maximum adsorption capacities and adsorption rate constants. Adsorption capacities increase with increasing adsorbent bed height and the rate constant decreases with increasing bed height. Mitali et al. (2007) [15] and Lugwisha and Lunyungu (2016) [16] made the same observations.

CONCLUSIONS

The purpose of this study is to improve the native Saharan diatomite's qualities for use in hydrogeology and the environment. We utilized multiple techniques, including XRD, FX, FTIR, SEM, apparent density, and porosity, to examine the composition and morphology of diatomite. The investigation indicates that thermal treatment can enhance the elevated carbonate content of natural diatomite. The examination indicated an increased silica percentage and porosity in the latter, accompanied by reduced carbonate content.

The diatomite has seen many alterations as a result of heat effects. As the silica phases liquefied, the apertures in the siliceous frustules typically enlarged. This increased the total porosity, particularly in the softer varieties, and resulted in the emergence of cristobalite.
The results indicated that calcined diatomite possesses significant adsorption ability for phosphates, and total nitrogen is present in contaminated water.
A comparison of the experimental and simulated breakthrough curves shows that the BOHART and ADAMS models, the WOLBORSKA model, and the CLARK model provide a satisfactory description of the experimental data.

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