Removal performance for thermotolerant coliforms and fecal streptococci from dairy effluents by Kenadsa's natural green clay (Bechar-Algeria) in a fixed-bed column

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Abstract

This present work is a part of the liquid discharges treatment topic by studying the removal performance for thermotolerant coliforms (FC) and fecal streptococci (F.Strep) by a local natural light green clay from *Kenadsa* (Bechar-Algeria) under continuous adsorption processes in a fixed-bed column. The study estimated the clay adsorbing efficiency by the adsorption technique for bacteria contaminating the dairy effluent by determining the bacterial load before and after treatment. The mean log counts per 100 ml for FC and F.Strep were assessed by MPN method on liquid medium. The clay material characterizations were made through X-ray diffraction, X fluorescence spectrometry and Fourier transform infrared spectroscopy analysis. Besides, some parameters were estimated such as the breakthrough time t_b (clay filter breakdown); the amount of the contaminating bacteria that was removed at the breakthrough time X_b and the exhaustion of disinfection capacity X_e ; the total amount of contaminating bacteria flowing through the column X_{total} ; and the total removal efficiency (Y). According to the XRD, XRF and FTIR results, the predominant mineral constituents were silicon dioxide, aluminum oxide, ferric oxide and magnesium oxide with rates of 59,44; 18,09; 7,79; and 3,87%, respectively, and hence, their classification among non-swelling clay minerals, illite is the major mineral group of this material. The results of the bacteriological analysis of raw dairy effluents showed an average bacterial load of 3,88 Log₁₀ and 4,1 Log₁₀ CFU/100 mL for FC and F.Strep, respectively, exceeding the thresholds set by the national and the international regulations. The results of the dairy effluents treated by the tested material have shown that the used clay has a relatively high adsorption property for the clay fixed-bed system (3 cm of bed height), expressed by a total removed efficiency Y (%) of FC and F.Strep used to evaluate the column performance ranging from 55 to 84%. It gives a higher log removal for FC and F.Strep (0.98–1.65 Log₁₀) reported from the first adsorption process, and a breakthrough time ranged from 100 to 250 min, which was inversely proportional to the initial bacterial load of discharges and also linked to the nature of the bacterial contaminants. When the breakthrough occurs earlier, the column service life will be shortened. For the studied parameters, the results of treated effluent complied with national and WHO regulations for unrestricted agricultural irrigation, otherwise, as authorized effluents to be discharged into nature without risks. These preliminary results are very promising at laboratory scale as an innovative green technology, treatment method respecting the environment and opens up prospects for the future, where the modification or the optimization of operating conditions such as the bed height of the fixed bed for adsorption, the volumetric flow rate or the clay structure like the particle size distribution of the adsorbents, known as one of the adsorbent classes endowed with an antimicrobial property, can improve the column performance, and further, the removal or even more the disinfection process by adsorption method.

Keywords Clay characterizations · Dairy effluents · Thermotolerant coliforms · Fecal streptococci · Fixed-bed adsorption process · Breakthrough time · Adsorption parameters · *Kenadsa* (Bechar)

Abbreviations

ADB (Rothe)	Azide Dextrose Broth
BCPL	Bromo Cresol Purple Broth w/ Lactose
C	The effluent contaminant concentrations at time t (Log ₁₀ CFU/L)

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C_0	The influent contaminant concentrations at time t_0 (Log_{10} CFU/L)
C_{ad}	The adsorbed concentration
CEC	The cationic exchange capacity
CFU	Colony forming unit
EVA Broth	Ethyl-Violet-Azide, Litsky
FC	Thermotolerant coliforms
F.Strep	Fecal Streptococci
FTIR	Fourier transform infrared spectroscopy
MPN	Most probable number
pH_{PZC}	PH at the point of zero charge
Q_v	The volumetric flow rate (mL/min)
t_{total}	The total flow time (min)
t	The flow time (min)
t_b	The breakthrough time
t_e	The exhaustion time
X_e (Log_{10} CFU)	The amount of the contaminating bacteria removed at the exhaustion of disinfection capacity in the column
X_b (Log_{10} CFU)	The amount of the contaminating bacteria removed at breakpoint in the column
X_{total} (Log_{10} CFU)	The total amount of contaminating bacteria flowing through the column
XRD	X-ray diffraction
XRF	X-ray fluorescence
Y (%)	Total removal efficiency

Introduction

Water is essential for life, but it is also essential for the industrial and agricultural development of human societies. Pollution, accidentally or voluntarily by certain chemicals of an industrial origin (hydrocarbons, phenols, dyes, industrial oils) or an agricultural origin (pesticides, fertilizers), has now become a crucial problem of great concern, as it is a source of environmental degradation and is currently of a particular interest both nationally and internationally (Benyagoub et al. 2018a).

Besides, various human activities have affected the environmental system, by producing wastewater containing high levels of pollutants, and in a direct or an indirect way resulting in a serious life-threatening problem such as global warming (El-Naas and Alhaija 2011). According to WHO (2019), by 2025, half of the world's population will be living in water-stressed areas. The safe management of wastewater by re-using it can yield multiple benefits to recover water, nutrients, or energy, including increased food production, which becomes an important strategy for many countries.

Today, the preservation of the environment and water resources depends mainly on the ability to clean wastewater

at a low cost before being discharged into nature (Kendouci et al. 2013). Many scientific research in dry countries focused on the optimization of wastewater treatment in order to take advantage of their hydric and agronomic features without endangering the receptive environment (Bouanani et al. 2020). The processes implemented in conventional facilities, which aim to reduce the pollutant load until reaching an acceptable level to the receiving medium, are generally costly and consist of mechanical, biological, or physicochemical methods, such as adsorption, precipitation, electrolysis, ion exchange, clotting or oxidation, and flocculation processes (Rodier 2009). Among these methods, adsorption is recognized as one of the most widely used methods in the world due to its effectiveness, and also to be an economical method to remove or even to reduce the concentration of metal ions or pollutants in general from surface waters/wastewater (Unuabonah et al. 2018; Meroufel et al. 2020). Adsorption is a process of material transfer between a liquid (or gaseous) phase loaded into an organic or an inorganic compound and a solid phase adsorbent. This capacity depends on the surface of the material and its specificity (Unuabonah et al. 2018).

Because of the abundance of clays on the earth's surface and due to their ability to undergo transformations in different ways, these solids are involved in many applications: pharmaceuticals, petroleum, chemical, wastewater treatment, catalysis, etc (Boudriche et al. 2021); consequently, clays have received considerable attention, especially as potential adsorbents for environmental research (Birhanu et al. 2020).

In Algeria, milk has an important place in everyone's diet, not only because of its richness in nutrients, but also because it is financially supported by the Algerian state (Amellal 1995; Benyagoub et al. 2017) which has experienced an increase in milk consumption that exceeds 160L/person/year (Benyagoub et al. 2018b), and the large part of the produced milk by replenishment of the milk powder as raw material is provided by the dairy industries and therefore results in an increase in discharged dairy effluents highly loaded with organic matter, where the volume that did not undergo any treatment and released into nature could constitute a threat to the ecosystem and to the public health (Benyagoub et al. 2018a).

As water of good quality is a precious commodity and available in limited amounts, it has become highly imperative to treat wastewater for the removal of pollutants (El-Naas and Alhaija 2011).

For that and in the context of water treatment, an experimental approach was done and aimed at evaluating the adsorbent efficiency of the clay fixed bed under dynamic conditions at atmospheric pressure for the removal of thermotolerant coliforms and fecal streptococci, by filtration of three samples of dairy effluents discharged from a small dairy industry located in Bechar (Southwest of Algeria).

Materials and methods

Dairy effluents Characterization

The dairy unit is located in Nif Errhaa-Ouakda (14 km north of Bechar-Southwest Algeria), a private investment inaugurated in November 2016. This unit produces an average of 15,500 L/day of pasteurized partially skimmed milk, and 5,000 L/week of fermented milk, depending on the availability of the raw material. It includes an administrative block, a manufacturing workshop with two cold rooms and a steaming room, three collection basins for liquid effluents from the industry. The dairy unit has initially generated 31 direct jobs and as many other indirect jobs in the form of contracts (Benyagoub et al. 2018a; Benyagoub 2019; Nabbou et al. 2020).

The industry discharges into the environment medium a volume of raw dairy effluents from 50 to 75 m³/Day, where the effluents' nature is mainly milk, cooling water, and chemical products (detergents, caustic soda, and nitric acid) used in the cleaning and disinfecting operation for equipment, and piping circuit of dairy industry (Nabbou et al. 2020).

In general, water sample collection is a delicate operation in which the greatest care must be taken. First of all, the sample must be homogeneous, representative, and obtained without modifying its physicochemical or microbiological characteristics (Rodier 2009). Necessary samples of raw dairy effluents for the adsorption test experiments and bacteriological analyses were collected according to the method described by Rodier (2009): in a plastic or glass disposable bottles and stored at +4 °C, then analyzed at most within 24 h from gathering. The various manipulations were done at the level of *Mohammed TAHRI* University of Bechar (Algeria).

The dairy effluents' samples were taken after completing the unit's production from the basins where the sterile glass bottle is immersed 30 to 50 cm down from the surface. A total of three samples were taken, the sample is immediately identified by a reference, then analyzed before and after treatment using the clay where the samples' pH was measured in situ using a pH meter (HANNA HI2210, Italy) (Nabbou et al. 2020) (Table 1).

Clay material characterization

The tested clay comes from the Kenadsa deposit. The latter is among the communes of the Wilaya of Bechar (Southwest of Algeria). It comes in the form of light green rock. First, the clay was ground with a ball grinder. Second, sifted with a stainless steel sieve to obtain an 80 µm

Table 1 Frequency and date of sampling of dairy effluents

Samples	Sampling date	pH value (Nabbou et al. 2020)
DE 1	March 12, 2019	6,11
DE 2	April 15, 2019	6,73
DE 3	April 30, 2019	7,15

DE (1, 2 and 3): Dairy effluent samples

granulometry powder, and third, washed by using the sedimentation method (Fig. 1a).

Thus, several techniques have been used in this study to determine the physical and the chemical properties of clays namely: X-ray diffraction (XRD) to determine the mineralogy of clays, X-ray fluorescence spectrometry (XRF) to estimate their chemical composition, infrared spectroscopy (FTIR Fourier transform infrared spectroscopy) to detect the functions of the clusters' structure, the pH at zero charge point (pH_{PZC}) to detect the surface charge of the clay particle, the ability to exchange (CEC) to estimate the theoretical power of cations fixation and the specific surface. FTIR's analysis of the clay was conducted using a NICOLET 6700 IR spectrometer.

XRD and XRF analyses were performed using a Philips X-type diffractometer (Magi XPRO) and a PANalytical device. The CEC cationic exchange capacity of the tested clay was determined by the methylene blue method according to Kahr and Madsen (1995) to determine pH at zero charge (pH_{PZC}) that corresponds to the pH for which the surface of the solid has a zero charge, using the method of the variation of pH which consists of placing 50 cm³ of NaCl solution (0,01 M) in closed vials and adjusting the pH of each between 2 and 12 per addition of the solution of NaOH or of HCl (0,1 N). Then, 0,15 g of material sample is added to each vial. The suspensions must be kept under continuous stirring at room temperature, during 48 h. The final pH is then determined. We traced the evolution of the final pH as a function of the adjusted initial pH. The pH_{PZC} is graphically obtained at the point where the first curve corresponding to the initial pH curve as a function of the final pH [Initial pH = f(Final pH)] intercepts the second curve [final pH = initial pH] (Orfao et al. 2006; Benselka 2015). Also, the pH_{PZC} can be mathematically calculated through the equation of a linear regression line.

Clay preparation method

The studied Kenadsa's natural clay as a raw material was purified by aqueous dispersion and decantation (Guiza et al. 2019). The clays' granules are calcined in a muffle

Fig. 1 Preparatory steps of calcined clay in the form of granules (Source: Original, 2019). **a** Method of sedimentation and drying of Kenadsa's natural green clay (Bechar-Algeria); **b** Calcination of clay in a muffle furnace; **c** Calcined clay

furnace under the following operating conditions (Fig. 1b): $T = 400\text{ }^{\circ}\text{C}$ for 1 h. The calcined clay is given in the Fig. 1c.

Adsorption test experiments in a fixed-bed column

The use of minicolumns in dynamic mode adsorption study constitutes a relatively fast, simple, and reproducible analytical method.

This method was used by Rosene et al. (1976); in this system, the used assembly is composed of a separations' minicolumn, a peristaltic pump which injects the effluent dairy sample to be treated with a flow rate 'Q' equivalent to 2 ml/min taken out in a sterile glass vial.

Noting that the volume to be poured for each operation is fixed to 100 ml for 50 min through the mass of the calcined clay granules equivalent to a very precise bed height placed in the column (Fig. 2).

The operation is carried out in a purification system which is characterized by:

- m (mass) = 11,20 g, and H (bed height) = 3 cm.

The recovered filtrate after filtration and the ones before the filtration process undergoes a series of bacteriological analyses to evaluate some essential adsorption parameters for the clay fixed bed.

Bacteriological analysis

The standard counting bacteria is a very important step during the water treatment process, as it allows to evaluate the effectiveness of various treatment stages.

The bacteriological analysis of the dairy effluents before and after filtration treatment that focused on the microbial

Fig. 2 Dairy effluents filtration using a clay fixed-bed adsorption system (Source: Original, 2019)

indicators of fecal pollution (thermotolerant coliforms and fecal streptococci) was carried out on the basis of standard methods furnished by the American public health association (Rice et al. 2017) and FUNASA-National health foundation (2013) as follows:

- Fecal coliforms (thermotolerant) subgroup of coliform bacteria which ferment lactose at $44,5 \pm 0,2\text{ }^{\circ}\text{C}$ within 24 h, and *Escherichia coli* is the main representative bacterium of this group and exclusively fecal origin. The detection and enumeration of thermotolerant coliforms was then carried out by the MPN method on BCPL medium (Lioflichem Diagnostici, Italy). The inoculated

Table 2 Maximum limit values and specific data for discharges of effluent, spills or deposits of any kind that do not pose a risk of toxicity or nuisance in the hydraulic public domain (Ministry of water resources and the environment of Algeria JORA n°30, 2013; Benyagoub et al. 2018a)

Bacteriological parameters	Maximum limit values (CFU/100 mL)
Fecal streptococci	10 ³
Thermotolerant coliforms	2.10 ³

Table 3 Bacteriological parameters of treated water according to WHO (1989) (Benyagoub et al. 2018a)

Bacteriological parameters	Limit values (CFU/100 mL)
Total coliforms	–
Thermotolerant coliforms	10 ³
Fecal streptococci	–

tubes are incubated at 44 °C for 24 to 48 h (AFNOR T 90–413, 1985).

- Detection and enumeration of fecal streptococci on azide dextrose broth (ADB Rothe) as a presumptive test) and EVA broth as a confirmatory test (Lioflichem Diagnostici, Italy) by the MPN method, usually used for the detection of *Enterococci* in water and sewage, where the inoculated tubes are incubated at 37 °C for 24 to 48 h (NF EN ISO 7899–1, 1999).

The results were recorded as colony forming units per 100 mL (Log₁₀ CFU/100 mL) by following McCrady's table (3 tubes per dilution) (Woodward, 1957; Tillett, 1987).

The analyzed bacterial parameters were interpreted on the basis of the limit thresholds of agro-food industry discharges given by the Algerian standards (JORA n°30, 2013), as well as those of the World Health Organization (WHO 1989), which specified the bacterial load limits of thermotolerant coliforms and fecal streptococci (Tables 2 and 3), in parallel

of bacteriological specifications for purified wastewater used for irrigation purposes (Table 4).

Clay fixed-bed efficiency: mathematical calculations

Clays, the main adsorbents used in water treatment, have many advantages allowing the elimination of a wide range of pollutants; not only different types of dyes, but also other organic and inorganic pollutants such as microorganisms, metal ions, pesticides, detergents, etc. The adsorption or retention ability of the clay was assessed by the (Ce/C₀) ratio evolution as a function of time of each bacterial parameter. This ratio represents the bacterial load of the filter at the outlet of the column on the initial bacterial load of the sample over time [Ce/C₀=f(t)]. The breakthrough time of a filter was calculated from the breakthrough curve which allows us to know how often the purification process can remain valid.

According to Akhigbe et al (2016) and Li et al (2018), breakthrough curves of effluent pollutant concentration against time were plotted from the results of the fixed-bed columns experiments. For the contaminating bacteria removal, the amount of bacterial parameter removed C_{ad} equal to (C₀–C) at breakpoint, X_b (Log₁₀ CFU) in the column was calculated using the following equation (Eq. 1):

$$X_b = \frac{Q_v}{1000} \int_0^{t_b} (C_0 - C) dT \quad (1)$$

where Q_v is the volumetric flow rate (mL/min), C₀ and C are influent and effluent contaminant concentrations (Log₁₀ CFU/L) at time *t* (min), *t_b* is the breakthrough time.

Similarly, the amount of the bacterial parameter removed at the exhaustion of disinfection capacity, X_e (Log₁₀ CFU) in the column was calculated using the following equation (Eq. 2) (Akhigbe et al. 2016):

$$X_e = \frac{Q_v}{1000} \int_0^{t_e} (C_0 - C) dT \quad (2)$$

Table 4 Bacteriological specifications for purified wastewater used for irrigation purposes (Ministry of water resources and the environment of Algeria JORA n°41, 2012)

Culture groups	Bacteriological parameters (Fecal coliforms (CFU/100 mL))
Unrestricted irrigation Culture of products that can be eaten raw	< 100
Vegetables that are eaten only cooked	< 250
Vegetables for canning or non-food processing	
Fruit trees	Recommended threshold < 1000
Crops and fodder shrubs	
Cereal crops	
Industrial crops	
Forest trees	
Floral and ornamental plants	

where Q_v is the volumetric flow rate (mL/min), C_0 and C (Log_{10} CFU/L) are influent and effluent contaminant concentrations at time t (min), t_e is the exhaustion time.

The total amount of contaminating bacteria flowing through the column X_{total} (Log_{10} CFU) can be calculated with Eq. (3):

$$X_{\text{total}} = \frac{C_0 Q t_{\text{total}}}{1000} \quad (3)$$

where the t_{total} and Q represent the total flow time (min) and the volumetric inflow rate (mL/min), respectively.

The total removal efficiency (Y %) of thermotolerant coliforms and fecal streptococci can be used to evaluate the column performance, as expressed in the following equation (Eq. 4):

$$\text{Total removal efficiency (Y)} = \frac{X_e}{X_{\text{total}}} 100 \quad (4)$$

Statistical analysis

The experiment was repeated twice to present the obtained results as means, calculated using OriginLab software (2018) from where graphical presentations were obtained in the form of curves and histograms.

Results

Clay material characterizations

The XRD diagram of the studied clay is presented in Fig. 3. Peaks of 9,974, 4,994 to 3,344, and 2,45 are, respectively, reflections (001), (002), and (131) of the illite (Nayak and Singh 2007). We also note the presence of quartz and dolomite as associated minerals. The reflections of quartz are manifested at 4,252, 3,326, 2,458, and 1,541 (Nayak and Singh 2007), while the peaks of the dolomite appear around 2,998 and 2,127 Å.

According to the XRD results, the predominant mineral constituents are silica and alumina: these elements form the structure of clay. However, we note that if we calculate the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (Table 5), we will find a value of 3,28 which justifies the nature of the collected illite clay whose structure corresponds to two silica layers for an aluminous layer (so-called 2/1 clay), which also has a very high silica content, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ values are generally between 2 and 4 for illite clay (Robert and Tessier 1974). The presence of potassium (K) and iron (Fe) in this type of clay shows the presence of illite. According to the literature (Pusino et al. 1989) and (Jouenne 1980), the iron is found in the form of oxy-hydroxides, namely goethite (FeOOH), and/or oxides such as hematite (Fe_2O_3) and maghemite (Fe_2O_3). A high percentage may exist in montmorillonites and illites but it is low in kaolins.

Fig. 3 XRD pattern of Kenadsa's natural green clay (Bechar-Algeria)

Table 5 Chemical properties of Kenadsa's natural green clay (Bechar-Algeria)

Element	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	SO ₃	Total
Content in (%)	59,44	18,09	7,79	0,44	3,87	0,03	1,16	7,45	0,12	1,06	0,04	99,99

The purpose of the FTIR infrared spectroscopy clay study is to determine the different chemical functions that are present on the surface of these solids. It is a complementary technique that generally focuses on the study of samples at molecular level. In the case of clays, it essentially reveals the presence of carbonates and of organic matter. It is often used to characterize the nature of adsorbent/adsorbed interactions. Figure 4 shows the infrared spectrum of the studied clay. Generally, the adsorption's band that appears in the interval ranging from 3700 to 3620 cm^{-1} corresponds to the vibrations of the structural hydroxyl groups (Farmer 1974; Horn 1998). The exact position of these bands and their intensities vary depending on the nature of the molecules' bonds. They appear in clay around 3607 cm^{-1} . The bands that appear approximately to 3430 cm^{-1} and 1630 cm^{-1} correspond, respectively, to the elongation and deformation vibrations of the hydroxyl group of adsorbed water (Horn 1998). They appear in clay around 1646 cm^{-1} . The characteristic bands of the deformation vibrations of the Si–O quartz link occur around 985 cm^{-1} (Bellamy 1975; Onal 2002). The infrared spectrum also shows the signals: 985, 836, 797, 694, and 515 cm^{-1} which correspond to the elongation vibration of Al–OH–Al, Si–O–Si, Si–O–Al/Al–Mg–OH, cristobalite, and Mg–OH groups (Onal 2002; Nabbou et al. 2019). The characteristic band at 797 cm^{-1} is not only attributed to Si–O–Al/Al–Mg–OH elongation vibrations, but it is also attributed to the presence of illite (Wolf 1963; Nayak and Singh 2007). The total absence of organic matter bands is noticeable around 2920 and 2850 cm^{-1} (Bellamy 1975).

Determination of cation exchange capacity of clay (CEC)

Cationic exchange capacity (CEC rate) is the number of negative charges likely to fix cations. The measurement of cationic exchange capacity was carried out by the methylene blue method (Ammann et al. 2018). The ability to exchange illite clays was between 10 and $40\text{ meq}/100\text{ g}$ (Morel 1996). The studied clay has a CEC of $9,6\text{ meq}/100\text{ g}$. This can be explained by the fact that natural clay has a relatively high degree of soluble salts (impurities) that prevent the complete saturation of its exchangeable sites. This value is included in the field corresponding to illite (mica). This result is in good agreement with those revealed by the X-ray diffraction analysis. The presence of the illite has been confirmed in the natural clay.

Determination of clay's pH_{PZC}

To determine the pH at zero charge, the final pH curve is firstly plotted according to the initial pH, and secondly, the right formed by the initial pH equal to the final pH. The intersection point between the two curves corresponds to the pH_{PZC} of the studied material. The surface is positively charged for pH lowers to the pH_{PZC} , while for higher pH value, the surface is negatively charged. According to Fig. 5, Kenadsa's natural green clay has an isoelectric point of 8,38. For a pH of a solution greater than the isoelectric point, the surface of the adsorbent is negatively charged which disadvantages the adsorption of bacteria leading to a low retention rate, while for a pH of a solution below the isoelectric point; the retention of bacteria is favored due to the difference in load with the adsorbent. This result corroborates those obtained by Smolik et al

Fig. 4 FTIR spectra of Kenadsa's natural green clay (Bechar-Algeria)

Fig. 5 pH_{PZC} of Kenadsa's natural green clay (Bechar-Algeria)

(1966), the zero load point of aluminosilicates (Al_2O_3 , SiO_2) was estimated at a pH between 6 and 7, and for the illite's pH_{PZC} was 8.

Based on the results of the physical characteristics of the studied clay, and hence their classification among non-swelling clay minerals, illite is the major mineral group of this material.

Bacteriological analysis

In this study, we evaluated the disinfectant power of local clay through a purification system based on the filtration of dairy effluent samples where bacteriological analyses of pre- and post-treatment discharges are used to assess the effectiveness of disinfection treatments. The results are given in the following curves.

The influent bacterial contaminants concentration (C_0)

Bacteriological analyses of dairy effluents can thus assess the risk due to the presence of contaminant or pathogenic microorganisms, which may be found in these discharges. The bacterial loads are given in the cited figure below (Fig. 6).

According to Fig. 5, we note that the analyzed dairy effluents were loaded with bacteria indicators of contamination where the bacterial load exceeds the thresholds set by Algerian and WHO regulations ($3.3 \log_{10}$ CFU/100 mL with an average load of thermotolerant coliforms and fecal streptococci for all analyzed samples of 3.88 and 4.1 $\log_{10}$ CFU/100 mL, respectively.

Fig. 6 The level of bacterial contaminants of the analyzed dairy effluents **FC**: Thermotolerant coliforms; **F. Strep**: Fecal streptococci; **DE**: Dairy effluent samples

The effluent bacterial contaminants concentration (C_e)

The analyzed dairy effluents after treatment by filtration process showed bacterial loads that meet the national and international requirement in terms of discharges.

At the first filtration, the bacterial load of the filtrate (DE f1) was $2.3 \log_{10}$ to $2.7 \log_{10}$ CFU/100 mL for thermotolerant coliforms, and $2.6 \log_{10}$ to $2.9 \log_{10}$ CFU/100 mL for fecal streptococci (Fig. 7). This treatment system had a significant retention capacity where the total removed efficiency Y (%) of thermotolerant coliforms and fecal streptococci used to evaluate the column performance were (83,54; 67,65; and 62,22%) and (67,58; 66,97; and 54,75%) for the dairy effluents samples 1, 2, and 3, respectively (Table 6).

Figure 6 shows a high adsorption power, three operating cycles as filtration frequency for the samples 1 and 2, and up to five operating cycles for the 3rd sample where the reduction rate of bacteria decreases after each filtration until the adsorption capacity of the clay fixed bed becomes zero, and no interaction will then take place after the obtained filtrate had as much load of contaminating bacteria as that of the raw dairy effluents (RDE).

Clay retention capacity

Clay minerals have several properties that are very cost-effective to be used as an ideal adsorbent. In this study, we considered testing the clay fixed-bed adsorption process (3 cm of bed height).

The breakthrough curve represents the adsorption kinetics of thermotolerant coliforms and fecal streptococci as a function of time (Fig. 8) by clay minerals, where at the first time of the adsorption process is great then decreases over time

Fig. 7 Clay retention capacity of thermotolerant coliforms and fecal streptococci by filtration using clay fixed-bed system. (1): DE1 sample; (2): DE 2 sample; (3): DE 3 sample; **DE**: Dairy effluents; **RDE**: Raw dairy effluents; **f** (1 to 7): Infiltration frequency; **FC**: Thermotolerant coliforms; **F.Strep**: Fecal streptococci

Table 6 Experimental results for thermotolerant coliforms and fecal streptococci removal by a local Kenadsa's natural green clay, under continuous adsorption processes in a fixed-bed column

Samples of dairy effluents	DE1	DE2	DE3
Bacterial parameter: Thermotolerant coliforms			
C_0 (log ₁₀ CFU/L)	39,5	40,8	36
t_b (min)	150	150	150
X_b (log ₁₀ CFU)	8,79	7,29	5,67
t_c (min)	300	300	350
X_c (log ₁₀ CFU)	19,8	16,56	15,68
X_{total} (log ₁₀ CFU)	23,7	24,48	25,2
Y (%)	83,54	67,65	62,22
Bacterial parameter: Fecal streptococci			
C_0 (log ₁₀ CFU/L)	43,8	43,6	35,8
t_b (min)	100	150	250
X_b (log ₁₀ CFU)	3,76	7,53	8,5
t_c (min)	300	300	350
X_c (log ₁₀ CFU)	17,76	17,52	13,72
X_{total} (log ₁₀ CFU)	26,28	26,16	25,06
Y (%)	67,58	66,97	54,75

until complete saturation of the filter where the C_e/C_0 ratio is equal to 1 at the maximum time of 200 min for samples 1 and 2, then for the sample 3 up to 300 min, and no more clay-bacteria interaction will take place.

The curve made it possible to determine the breakthrough time for the bacterial parameters, thermotolerant coliforms, and fecal streptococci which was in the order of (150 and 100 min), (150 and 150 min), and (150 and 250 min), respectively, for samples 1, 2, and 3 (Table 6).

Table 6 provides the performance of the column for thermotolerant coliforms and fecal streptococci removal at a fixed flow rate.

Discussion

Outbreaks of the water-borne disease continue to occur, sometimes leading to lethal consequences which according to the World Health Organization (2000); 3,4 million people, mostly children, die annually from water-related diseases such as cholera, diarrhea, dysentery, food poisoning, typhoid, and also many other pathologies (WHO 2000), where the water-related pathogens are the cause of diseases leading to morbidity and to mortality in developing countries (Unuabonah et al. 2018; Benyagoub et al. 2018c). Hence, the importance of continuously monitoring the contamination level of the discharged water into nature (Kendouci et al. 2019). Thus, this study fits this context. According to Unuabonah et al. (2018), the operation of the disinfection of contaminated water could occur by chemical

Fig. 8 Breakthrough curves for the adsorption of thermotolerant coliforms and fecal streptococci. **(1):** DE sample 1; **(2):** DE sample 2; **(3):** DE sample 3; **DE:** Dairy effluents; **FC:** Thermotolerant coliforms; **F. Strep:** Fecal streptococci

and/or physical means namely adsorption, distillation, and filtration as physical processes, activated sludge as a biological process, and physicochemical processes like flocculation, chlorination, and zonation (Ma et al. 2014). Note that chemical agents such as chlorine and its compounds are most widely used in water treatment due to their efficiency, their low cost, and their additional protection against bacterial re-growth (Amin et al. 2014). However, the addition of these chemicals changes the water taste and also reacts with various constituents of natural water to form disinfection by-products, many of which are considered as carcinogenic (Villanueva et al. 2007).

This has always emphasized the need to develop a water purification strategy and move toward efficient purification techniques, for example, the use of materials that are available and less expensive known for their disinfectant properties.

Membrane filtration, which is very effective in disinfecting water, has a fouling drawback that requires a frequent membrane replacement and therefore increases the cost of the entire water treatment process.

On the other side, the adsorption technology is considered as one of the most practical and efficient approaches for the treatment of numerous types of wastewaters due to its simplicity, high efficiency, low operating cost, ease to regenerate the adsorbent, and scaling-up. In fact, it has been considered by many to be superior compared to other physical and chemical technologies (Nassar et al. 2012; El-Naas and Alhajja 2011).

This process has a competitive advantage compared to other purification techniques that do not generate by-products. Among the adsorbents with environmental remediation properties, clays' minerals are considered to be excellent adsorbents for the elimination of bacteria in water (Muter et al. 2012). They have large specific surfaces, high porosity, surface charge, and surface functional groups that qualify them as useful adsorbents (Yuan et al. 2013).

Since the treatment operation is not functional at the studied dairy industry, the proliferation of contaminant bacteria is justified, where the bacteriological analysis results of the raw dairy effluents showed a significant bacterial load. These results are in agreement with a previous study carried out by Benyagoub et al. (2018a) on dairy effluents discharged from the same studied dairy industry where a load of thermotolerant coliforms and fecal streptococci were in the range of $2.07 \log_{10}$ to $5.2 \log_{10}$ CFU/100 mL, and from $1.84 \log_{10}$ to $5.9 \log_{10}$ CFU/100 mL, respectively, and remains lower than that reported by Hamdani et al (2005) in which the studied dairy effluents during a year have thermotolerant coliforms and fecal streptococci loads ranging from 4.29 to $4.6 \log_{10}$ CFU/mL.

According to the study conducted by Kjellander (1960) on the Enteric streptococci as indicators of fecal contamination

of water, notes that fecal streptococci survive longer than coliforms. This may explain the difference in bacterial load, where the level of bacterial contamination is not only limited by the contamination origin based on the FC/F.Strep ratio report, but also linked to the organic matters and to the physicochemical parameters that contribute to the bacterial activity such as temperature and pH (Larif et al. 2013).

This can be explained by the lack of treatment which leads to the proliferation of different microorganisms. Besides, the wastewater is considered as the optimal environment for microbial growth (Benyagoub et al. 2018a). Noting that coliforms can be found in the aquatic environment, soil, and vegetation. These bacteria are commonly present in large quantities in warm-blooded animal feces. Although coliforms themselves do not usually cause serious illness (Sumampouw and Risjani 2014).

Regarding the column performance, the obtained filtrate by filtration treatment of dairy effluents has shown a high reduction in bacterial load ranging from 55 to 84% of the initial charge of dairy effluents, and that the filter can be functional for two to five times as filtration frequency resulting in a variable breakthrough time that depends on the initial bacterial load and the bacterial species. These results remain inferior compared to the study results reported by Khamkure et al (2016) on the effect of clay soil content on fecal bacteria removal from the municipal wastewater in an intermittent media infiltration system, where the mixture of clay soil and filter media in a ratio of 75/25 gave the best performance for FC removal, and the average FC reductions for sand, zeolite, vermicompost, and charcoal were 94,4; 82,2; 93,8; and 99,6%, respectively.

The chemical composition results of the studied Kenadsa's natural clay were closer to those given by Guiza et al (2019) for natural clay composition, in which the major components were SiO_2 (59,44 vs. 47,7%), Al_2O_3 (18,09 vs. 18,71%), and Fe_2O_3 (7,79 vs. 12,37%), respectively, and higher than those cited by Dehmani et al (2020), for SiO_2 (59,44 vs. 38,74%), Al_2O_3 (18,09 vs. 10,6%), and Fe_2O_3 (7,79 vs. 6%), but for the calcium oxide (CaO), the Kenadsa' clay had a very low mass (0,44 vs. 16,8).

Clays are generally characterized by the presence of three main active sites located at the edge of the sheets, the two surface hydroxyl groups which are the silanol groups (Si–OH), the aluminol groups (Al–OH), and the Lewis acids (Farquhar et al. 1997). In addition, the presence of the reaction sites on the side faces of the sheets resulting from the hydrolysis of the aluminol and silanol bonds. These two hydroxyl groups can capture or give up a proton depending on the pH of the medium. The aluminol groups are the most favorable sites for the adsorption of anions due to the large presence of oxygen atoms compared to the silanol sites. In an acidic medium, these sites are characterized by the presence of positively charged functional groups

(AlOH^{+2}) allowing the retention of anions. However, in a basic medium, the charge of these sites becomes negative which causes an electrostatic repulsion between these sites and the anions. The presence of FeOH^{+2} functional groups resulting from the isomorphic substitution of aluminum by iron may also have favorable sites for adsorbing anions. Iron oxide and aluminum oxide are among the adsorbents which can be shown a high affinity to anions.

Since teichoic acids as polymers of glycerol and ribitol linked to PO_4 groups are connected to peptidoglycan or plasma membrane lipids (lipoteichoic) (Meyer et al. 2004), they are negatively charged in which bacteria can interact with clay minerals (Ahmad et al. 2013; Akhigbe et al. 2016). Besides, according to Alimova et al (2009), evidence suggests further that the interactions between bacteria and clay particles are beneficial to bacteria, clay particles may protect bacteria against dehydration and ultraviolet light. Also, clays can act as a source of minerals and cations. A previous study found that the clay improves the endurance and activity of pathogenic *E. coli* O157: H7 strain and other coliforms. In more than 500 days of the frozen stored soil, these bacteria are still present in 37% of tested samples. Moreover, these bacteria stop growing and multiplying in dairy effluents microcosms with or without circulating aerators (Sumampouw and Risjani, 2014), and according to Alimova et al. (2009), the knowledge of these interactions is still far from complete.

In this study, we measured the pH corresponding to the zero charge point of Kenadsa's natural green clay which was 8,38. While, strong adsorption was observed for the dairy effluents to be treated having a pH value below the pH_{PZC} of the used illite. The surface of the clay is positively charged, which can improve the absorption of bacteria. A literature and bibliographic search has revealed many studies on clay and modified clay minerals namely pyrophyllite with a mineral composition $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$, clay polymers that have been used, and also had a strong antimicrobial activity against Gram-positive and Gram-negative bacterial strains (Kang et al. 2013); Kaolinite is revealed as a better adsorbent of *Pseudomonas putida* compared to montmorillonite (Jiang et al. 2007) where these activities depend on several factors such as the surface and particle size of the adsorbent as well as their surface charges (positive charge) and the narrow particle size distribution of modified clay-based adsorbents.

Regarding the elements' composition, clays are hydrated alumina silicates (kaolinites, smectites, illites, montmorillonites, beidellite), natural minerals from the environment, composed of particles smaller than two-thousandths of a millimeter. The clay particles are able not only to bind bacteria by physical processes that they cannot defend themselves but also easily bind the bacterial toxins at the edge, inside, or between their thousands of ultramicroscopic layers, and help remove it from drinking water (Allègre 2012). According to

Alimova et al (2009), the large surface area of clay particles promotes the surface adhesion and clumping of bacteria.

The solid adsorbents and microbial cell surfaces play an important role in determining the adhesion of bacteria to the surfaces of the materials, which is an essential step in understanding the mechanism of removal of these bacteria from water. Noting that microbial adhesion and microbial control are the two main different water disinfection mechanisms (Unuabonah et al. 2018).

According to Unuabonah et al. (2018), the adhesion that was required as the first step in the elimination of bacteria is controlled by the chemical and physical interactions between the surface of the material and the bacteria. These interactions may be attractive or repulsive as a function of the interaction complex of chemical properties between bacteria and substrate surfaces, and the aqueous phase (Katsikogianni and Missirilis 2004; Hori and Matsumoto 2010).

The bacteriostatic composites of the clay prepared by Unuabonah et al. (2017) were found to have a positive charge due to the presence of ZnO in the clay mineral phase at a pH value below to the isoelectric point of the pH of ZnO (pH 9–10). The authors suggest that this electrostatic interaction between the bacteria and the modified clay mineral occurs in a pH value ranging from 4 to 8 in which the bacteria have a negative charge due to the presence of PO_4^{3-} and COO^- on its surface, which interacts with the positive charge on the surface of modified clay adsorbents through an electrostatic mechanism.

Also, according to the president of Human Clay society; Allègre (2012), the experiment carried out at the Microbiological Research Institute of Mitry-Mory, in the Paris region, showed that 25 g of illite clay could eliminate from half a liter of water seeded with 10^8 CFU/mL 92,6% of *Escherichia coli*; 87,3% of *Enterococcus hirae*; 99,7% of *Staphylococcus aureus*, and 95,5% of *Pseudomonas aeruginosa* (pyocyanic), the terror of hospitals. Other research confirms that clay particles can also catch viruses, and according to hydrology and water experts, a practice related to covering the surface of the water with a thin layer of green clay powder, and as soon as it falls to the bottom, the water can be drinkable. This is often carried out in poor communities worldwide to treat local water (Allègre 2012).

In addition to what has already mentioned before, various factors influence the adhesion of bacteria to the adsorbent surfaces or even more their lysis effects, in which the specific surface area is a key parameter for adsorption (Li et al. 2018). They include the properties or characteristics of bacteria, the properties of the adsorbent surface (surface chemistry, surface charge, and composition), where the role of Al^- and Fe^- rich silicates in the attachment of microbial cells to mineral surfaces has been explored, and the large surface area of clay particles promotes surface adhesion and clumping of bacteria, also, the environmental

properties (which can be proteins of the serum, roughness, and hydrophobicity of bacteria) and the flow conditions if the interaction is carried out for example in a fixed-bed mode (Katsikogianni and Missirilis 2004; Kouider et al. 2007; Di Bonaventura et al. 2008; Alimova et al. 2009).

The interest given to clays is justified by their qualities of high specific surface area, a cation exchange capacity, wide availability, and low cost (Saoudi and Hamouma 2013). In our case, the design and preparation of clay as a calcined granule has greatly improved its usefulness in disinfecting water.

Finally, we must focus on two essential points: First, the regeneration of the saturated adsorbent during the scaling-up by moving from the laboratory stage to the industrial scale, which can be considered as waste and its disposal, cannot be an economical option. This may include chemical, biological, or thermal way as practical methods, and according to El-Naas and Alhaija (2011), the most common methods consist of temperature changes (thermal swing adsorption) and changes in pressure (pressure swing adsorption); Second, the studied dairy industry should establish a program to limit the volume and pollutant load of discharged dairy effluents (Hamdani et al. 2005; Benyagoub 2019).

Conclusion

The polluted water decreases its ability to be used downstream and threatens public health and aquatic ecosystems, reducing the available volume and increasing competition for sufficient supply. Therefore, it is essential to limit pollution as much as possible by emphasizing all possible methods and means for liquid discharges' treatment.

This is the aim of this study to highlight the treatment of dairy effluents with natural green clay as a less expensive and available material. The obtained results were very promising where it shows a high reduction of bacterial indicators of water pollution with a possibility to reuse the clay fixed-bed adsorption system 2 to 5 more times in which the total removed efficiency Y (%) was ranging from 55 to 84% which gives a higher log removal for FC and F.Strep ($0,98$ – $1,65 \text{ Log}_{10}$) reported from the first adsorption process. For the studied bacterial parameters, the results of treated effluent complied with national and WHO regulations for unrestricted agricultural irrigation, otherwise, as authorized effluents to be discharged into nature without risks.

The natural clay that we used has shown its high adsorption capacity by retention of the bacterial contaminants. We note that under the tested conditions, the initial bacterial load of the dairy effluents was considered as a limiting factor in this type of treatment (Proportional function relationship). When the bacterial load of the dairy effluents is higher, consequently, the breakdown time of the filter will be short, and

then its clog-up is faster. This means that the filter will be less efficient. However, it is probably that the clay adsorption efficiency may vary based on the initial bacterial load and the adsorbent dosage.

The ability of Kenadsa's natural green clay in decreasing the bacterial contaminants loads from the dairy effluents has been proved and may solve the issues of agro-food liquid effluent discharges, which constitute a risk to human health and the environment.

These results showed a relatively good performance for the removal of FC and F.Strep compared to the mass of adsorbent used and the initial bacterial load of the dairy effluent.

In conclusion, the adsorption process with clays can be a simple alternative, selective, and economically acceptable for conventional biological treatment. For that, we suggest a better exploitation of these available materials in the studied area. More experiments are required to identify other properties that may be profitable and more money gaining in water treatment processes.

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Authors' contributions Data gathering and idea owner of this study: N.N; E.B * Collection of Dairy effluents samples/ Bacteriological analysis: E.B * Collection and preparation of clay/clay material characterizations: N.N; M.Bou; M.Ben. * Data analysis and mathematical calculations: N.N; E.B * Writing of the original manuscript/ Plotting curves: E.B * Manuscript review: N.N; M.Bel. All authors have read and approved the final manuscript.

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Data availability The datasets used and/or analyzed during the current study are available from the corresponding author/co-author on request.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval This study complies the Algerian ethical standards. However, this article does not contain any studies with human participants or animals performed by any of the authors.

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