Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1018331

57 (2016) 8183–8193
April

Taylor & Francis
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Dairy wastewater treatment by chemical coagulation and adsorption on modified dried activated sludge: a pilot-plant study

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Received 8 September 2014; Accepted 6 February 2015

ABSTRACT

Dairy industries and milk processing plants normally discharge their wastes directly to the close surroundings, generating environmental nuisances. Consequently, dairy wastewater deserves special attention since its levels of potential contaminants typically exceed those levels considered hazardous for domestic wastewater. At present study, performance of conventional chemical coagulation using poly aluminum chloride as an inorganic pre-polymerized coagulant (at various pH and coagulant dosages) and adsorption process by modified dried activated sludge (with $ZnCl_2$) for treatment of real dairy wastewater was investigated. Maximum removal efficiency of pollutants (BOD_5 and chemical oxygen demand (COD)) by chemical coagulation process was achieved at initial pH 8 and coagulant dose 100 mg/L in 60 min. In addition, optimum conditions for adsorption process were found to be: initial pH 6, adsorbent dose of 7 g/L, and contact time 90 min. The biosorption equilibrium data were fitted by Freundlich isotherm. Furthermore, according to the thermodynamic properties, ΔG°, ΔH°, and ΔS°, adsorption of COD onto modified dried activated sludge was spontaneous, endothermic, and feasible in the temperature range of 298–318 K.

Keywords: Dairy wastewater; Coagulation; Adsorption; Activated sludge

1. Introduction

In most developing countries including Iran, the production of dairy wastewater has increased due to the steady rise in demand of milk and dairy products. Dairy wastewater mainly originates from the processed wastewater due to the non-accidental losses of milk or dairy products, which is mixed with waters produced in various processing units as well as with water generated from living area [1–3].

In dairy industries, water has been a key processing medium. Water is used throughout all steps of the dairy industry including cleaning, sanitization, heating, cooling, and floor washing—and consequently, the requirement of water and wastewater generation is very high (approximately 0.2–10 L of waste per liter of processed milk). Dairy wastewater is distinguished by the high organic matter (chemical oxygen demand (COD) and five-day biochemical oxygen demand (BOD_5) contents), high levels of dissolved or suspended solids including fats, oils and grease, nutrients

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such as ammonia or minerals and phosphates and it is also malodorous because of the decomposition of some of the contaminants causing discomfort to the surrounding population, therefore requiring proper attention before final disposal to environment [4,5]. Furthermore, the wastewater is characterized by extensive fluctuations in flow rates, related to discontinuity in the production cycles of different products. The highly variable nature of dairy wastewaters in terms of volume and flow rates, and also in terms of the pH and suspended solids content, makes it difficult to choose an effective wastewater treatment regime [6].

Various methods have been used for dairy wastewater treatment (such as membrane systems, nanofiltration, and electrocoagulation processes [7–9]; nevertheless, dairy wastewaters are generally treated using aerobic and anaerobic biological methods such as activated sludge process, aerated lagoons, aerobic bioreactor, trickling filters, sequencing batch reactor, anaerobic sludge blanket reactor, anaerobic filters, biocoagulation, membrane bioreactor, etc. [6,10–13]. Aerobic biological processes are highly energy intensive, whereas anaerobic treatment of dairy wastewater reflects very poor nutrient removal, and effluents treated by anaerobic biological processes require supplementary treatment [9,14]. On the other hand, the physical/chemical methods that have been proven to be successful are coagulation/flocculation [15,16].

Chemical coagulation of dairy wastewater has also been studied by adding aluminum salts and polymer compounds, and a maximum COD removal efficiency of 45–75% has been reported [17]. Poly aluminum chloride (PACl) is an inorganic pre-polymerized coagulant which is commonly used as a flocculant to coagulate small particles into larger flocs that can be efficiently removed in the subsequent separation process of sedimentation and/or filtration. Much attention has been paid to PACl in recent years because of its higher efficiency and relatively low costs compared with the traditional flocculants [18,19]. On the other hand, PACl has become one of the most effective coagulant agents in water and wastewater treatment facilities with various applications, including removal of colloids and suspended particles, organic matter, metal ions, phosphates, toxic metals, and color [20–22]. Kushwaha et al. [1] employed coagulation by PACl for treating the simulated dairy wastewater and found 69.2% reduction in COD at 300 mg/L coagulant dosage.

Among different tertiary treatment processes, adsorption process has been found to be attractive for the removal of organic matters from aqueous environments. Activated carbon (AC) is usually used as an efficient adsorbent for the treatment of various types of wastewaters. Nevertheless, some investigators have utilized several low-cost adsorbents like bagasse fly ash, coal fly ash, rice husk ash, etc. for the treatment of a wide variety of wastewaters.

Kushwaha et al. [1] employed commercial AC and bagasse fly ash for the treatment of synthetic dairy wastewater. Optimum conditions were found at initial pH 4.8, adsorbent dose of 20 g/L for commercial AC, and 10 g/L for bagasse fly ash and contact time 8 h [9]. Rao and Bhole [23] used some low-cost adsorbents along with powdered AC for the treatment of dairy wastewater. PACl was found to be better in lowering total dissolved solids than other pretreated adsorbents like straw dust, saw dust, bagasse, coconut coir, and fly ash [23]. Sarkar et al. [4] employed coagulation by chitosan followed by adsorption with powdered AC as pretreatment steps before treating the dairy wastewater by membrane separation method. During adsorption step, powdered AC showed a maximum COD removal of 68% at pH 4, adsorbent dose of 1.5 g/L, and contact time of 1.5 h for dairy wastewater having an initial COD of 2,000 mg/L [4].

However, many combined processes are suggested these days. Therefore, this study aimed to investigate the performance of conventional chemical coagulation and adsorption processes for treatment of real dairy wastewater and finally to an acceptable level that can be discharged to environment with minimal adverse effects. Sequence of these processes can enhance removal efficiency of various pollutants present in dairy effluents. Consequently, several critical aspects regarding the effects of pH, coagulant dose (PACl), reaction time, dose of adsorbent, and temperature on the pollutants removal efficiency from real dairy wastewater are explored.

2. Materials and methods

2.1. Chemicals and analytical measurements

Raw wastewater used in this study was collected weekly from a dairy factory in Iran (Sistan and Baluchestan province, Zahedan city), with 27,000 (mean value) kg milk per day processing capacity. All the chemicals in this study were of extra pure or analytical grade. COD, BOD_5, total solids (TS), total suspended solids (TSS), total nitrogen, conductivity, total and fecal coliforms, and pH determinations were performed according to the standard methods [24]. COD was measured using COD reactor and direct reading spectrophotometer (DR/5000, HACH, USA). Five-day biochemical oxygen demand was determined by the manometric method with a respirometer Oxi-Top system (WTW). Total Kjeldahl nitrogen (TKN) was determined by using the standard Kjeldahl method. The pH and electrical conductivity (EC) were adjusted to a desirable value using NaOH or H_2SO_4, and NaCl, and measured using a pH meter model UB-10 (Ultra Basic, US) and a conductivimeter model Cond 3110, respectively.

2.2. Chemical coagulation process

Jar test is the most widely used method for evaluating and optimizing the coagulation–flocculation processes. This study consists of batch experiments involving rapid mixing, slow mixing, and sedimentation. Standard jar tests were conducted on a program-controlled jar test apparatus (Phipps and Bird jar) at 22 ± 2°C of room temperature for optimization of the pH and coagulant dosages. Firstly, optimization of pH (2–12) at a fixed coagulant dose of PACl (50 mg/L) was performed. Next, during the rapid stirring, predetermined amount of coagulant was dosed to give a certain PACl dose, ranged from 5 to 1,000 mg/L as Al (at an optimum pH). At present study, the intensity and duration of both rapid mixing and slow mixing were fixed, respectively, at 130 ± 5 rpm for 2 min in the case of rapid mixing and 40 ± 2 rpm for 25 min in the case of slow mixing for flocculation. The duration of sedimentation was kept constant at 30 min. The levels of mentioned parameters have been chosen according to conventional chemical coagulation process in water and wastewater treatment. At the end of the settling period, water samples were taken from the supernatants and important parameters including COD, BOD_5, TS, TSS, TKN, total phosphorus (TP), total coliform, fecal coliform (FC), EC, and turbidity were determined. The percentage removal of pollutants was calculated using the following relationship:

$$\% = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

where C_0 and C_e are initial and effluent concentration of pollutants (mg/L).

2.3. Adsorption process

After chemical coagulation of dairy wastewater, the supernatants were used for adsorption studies by modified dried activated sludge under various variables to obtain optimum conditions.

2.3.1. Adsorbent preparation

Activated sludge was collected as slurry from the sludge return line of the wastewater treatment plant in a municipal wastewater treatment plant (Zahedan, Iran). The characteristics of the sludge used in the experiment are shown in Table 1. Activated sludge was dried at 105°C for 24 h in a hot air oven to reach a constant weight and then sieved through a 70–60 standard mesh (0.21–0.25 mm). Then for chemical activation of adsorbent (dried activated sludge), a mixture of 250 g of powdered adsorbent, 110 g of $ZnCl_2$ and 110 g of water was kept overnight, and then the mixture was calcinated at 350°C. Then, chemically pretreated activated sludge was washed with water and dried. Subsequently, the adsorbent was washed and again dried at 105°C for 24 h.

Table 1
The characteristics of the sludge used for adsorbent preparation

Parameter	Characteristics
Sludge type	Return line
Suspended solids	2.8 g/L
Settleable solids after 30 min	346 ml/L
Sludge age	14 d

2.3.2. Batch adsorption experiments

For each experiment, a known amount of the adsorbent (powder of modified dried activated sludge) was introduced into 1 L flasks in which 1,000 ml of the dairy effluent after chemical coagulation (first step) was already present. This mixture was kept in a temperature-controlled shaker at a constant speed of 150 rpm at a pre-decided constant temperature for 4 h. The adsorbent was separated from the wastewater after 4 h and the solution analyzed for COD, BOD_5, TSS, TKN, TP, and turbidity.

Dosage study was carried out by varying the dosages of adsorbent in the range of 0.5–25 g/L at the optimum pH and 298 K. The adsorption of pollutants by the adsorbent was studied over a pH range of 2–12 at 298 K. The initial pH of the solutions was adjusted using 1 N aqueous solution of either H_2SO_4 or NaOH. The amount of adsorbed pollutant, q_e (mg/g), under different conditions was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{2}$$

where C_0 and C_e are the initial and equilibrium liquid phase concentration of pollutant (COD and BOD_5) (mg/g), respectively. V is the volume of the solution (L) and M is the amount of adsorbent used (g).

Isothermal experiments were performed at 298, 303, 308, 313, and 318 K with M values of 0.5–10 g/L at optimum initial pH for two important pollutants including COD and BOD_5. The adsorbents were separated from the wastewater after 4 h and analyzed for C_e. Finally, the equilibrium adsorption uptake, q_e (mg/g), was calculated using the upper equation.

3. Results and discussion

3.1. Wastewater characterization

Dairy wastewater contains milk solids, detergents, sanitizers, milk wastes, and cleaning water and also has a typical white color. It is characterized by high concentrations of nutrients, and organic and inorganic contents. Significant variations in COD (80–95,000 mg/L) and BOD_5 (40–48,000 mg/L) have been reported by various investigators of dairy wastewater [25,26].

Table 2 presents the real dairy wastewater characteristics prior to any treatment, after 3 h settling time and the guidelines from Iran for effluent discharge in the sewage urban works. The values of the pollution parameters were lowered after 3 h of preliminary settling time; nevertheless, the comparison of these values showed that important parameters including COD, BOD_5, TSS, total, and FC bacteria were very much greater than standards recommended by Iran (Table 2). The high BOD_5 and COD values indicated that it is heavily contaminated with organic matter. Consequently, the dairy effluent needed to be treated before discharge to environment. In addition, BOD_5/COD ratio was used as biodegradability indicator, so higher BOD_5/COD ratio reveal higher biodegradability of wastewater.

3.2. Chemical coagulation by PACl

Coagulation–flocculation is one of the most important physicochemical processes in treatment of industrial wastewaters to decrease the solids (suspended and colloidal) responsible for turbidity of the wastewater and also for the reduction of organic matters which contributes to the BOD_5 and COD content of the wastewater [15,16]. Addition of various coagulants involves destabilization of the particulate matters present in the wastewater, followed by particle collision and floc formation which results in the sedimentation or flotation.

3.2.1. Effect of initial pH of solution

At present study, PACl was used as the main coagulant for treating of real dairy wastewater. PACl is one of the most commonly used polymeric coagulants used in wastewater treatment. Fig. 1 represents the effect of initial pH on the pollutants removal. It is observed that as the initial pH of wastewater was increased, the pollutants removal increased up to pH 8.0 giving maximum removal efficiency of 77.12, 82.25, 88.58, 71.41, and 65.2% for COD, BOD_5, TSS, TP, and turbidity, respectively, and beyond pH 8.0, pollutants removal decreased. In addition, maximum removal efficiency for TKN was obtained at initial pH 10.0.

For pH > 8, speciation of Al(III) shows that the aluminum present in the water is in the form of $Al(OH)_4$ ions. These ions reduce the pollutants removal by PACl due to electrostatic repulsion between negatively charged colloidal particles present in the dairy wastewater and $Al(OH)_4$ ions [27]. Similar findings were reported by Kushwaha et al. [1] on dairy wastewater

Table 2
Characteristics of the raw dairy wastewater used for this study

Parameters	Raw wastewater, Mean ± SD	3 h settled wastewater, Mean ± SD	Permissive levels (Iran Standard for discharge to surface waters)
Total COD (mg/L)	2,073 ± 437	1,832 ± 365	60
Total BOD_5 (mg/L)	926 ± 274	803 ± 136	30
BOD_5/COD	0.45	0.44	–
Total solids (TS) (mg/L)	1,823 ± 371	1,372 ± 147	–
Total suspended solids (TSS) (mg/L)	534 ± 127	318.4 ± 27.3	60
Total Kjeldahl nitrogen (TKN) (mg/L)	87.6 ± 16.3	65.5 ± 15.4	2.5
Total phosphorus (TP) (mg/L)	24.7 ± 3.8	18 ± 8.5	6
Oil and grease (mg/L)	218 ± 132	207 ± 114	–
Total Coliform (MPN/100 ml)	$4.26 \times 10^6 \pm 2.3 \times 10^5$	$3.27 \times 10^6 \pm 1.4 \times 10^5$	1,000
Fecal Coliform (MPN/100 ml)	$3.21 \times 10^6 \pm 1.4 \times 10^5$	$2.52 \times 10^6 \pm 6.8 \times 10^4$	400
Conductivity (µS/Cm)	2,023 ± 472	1,939 ± 214	–
pH	8.13 ± 0.52	8.03 ± 0.86	6.5–8.5
Turbidity (NTU)	623 ± 327	437 ± 208	50

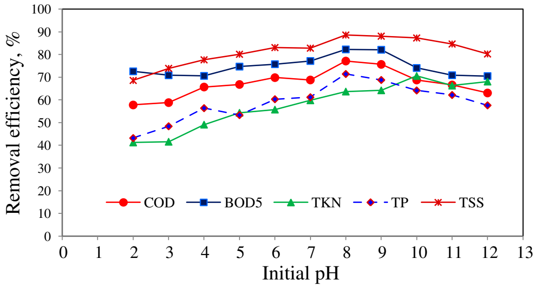

Fig. 1. Effect of initial pH on pollutants removal from real dairy wastewater (by PACl at dosage = 50 mg/L).

treatment by inorganic coagulants. Consequently, initial pH 8.0 was taken as optimum pH, for further experiments.

Fig. 2 shows the parity plot between initial pH and final pH of solution for the treatment of real dairy wastewater at various initial pH. It may be seen that final pH is lower than initial pH in full studied range. It is well known that addition of PACl leads to release of H^+ ions which decrease the pH of the solution [27–29]. Furthermore, removal of milk proteins and other components from dairy wastewater decreases the pH [1]. Additionally, as it can be seen from Fig. 2, conductivity of solution was decreased with increasing of initial pH of solution.

3.2.2. Effect of coagulant dose

Fig. 3 represents the effect of coagulant dose on pollutants removal efficiency of real dairy wastewater at optimum pH equal 8.0. It is clear from Fig. 3 that removal efficiency for most of pollutants first increased then decreased and again increased by increasing PACl. Furthermore, it can be seen that addition of PACl to real dairy wastewater decreased the final pH and maximum reduction observed at coagulant dose 1,000 mg/L. Final pH of wastewater decreased from 7.92 to 3.56 by increasing the coagulant dose of PACl from 100 to 1,000 mg/L. The colloidal nature of dairy wastewater is mainly due to the casein (milk protein). Dairy wastewater has the isoelectric point (pHiso) around 4.2 [1,30]. The milk proteins contained in the dairy wastewater are negatively charged at pH > pHiso and get removed by positively charged aqua aluminum cations formed from PACl.

It is shown that at lower doses of the PACl (5 mg/L), COD removal efficiency reached a maximum of 8.09%; BOD_5 removal efficiency reached a maximum of 11.23%; TKN removal efficiency reached a maximum of 26.8%; TP removal efficiency reached a maximum of 21.32%; TSS removal efficiency reached a maximum of 32.05% and turbidity removal efficiency reached a maximum of 43.3% and as it shown in Fig. 3, the efficiency of the process increased with increasing dosages of coagulant (PACl).

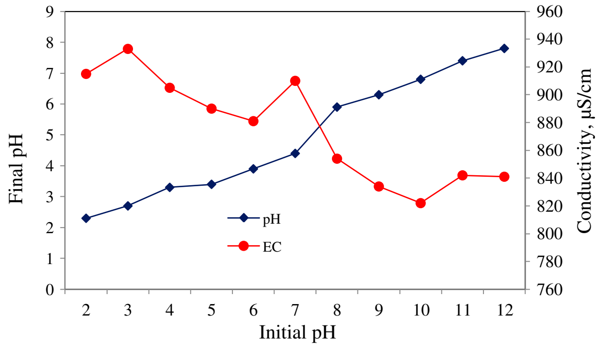

Fig. 2. Effect of initial pH on final pH and conductivity of real dairy wastewater (PACl dosage = 50 mg/L).

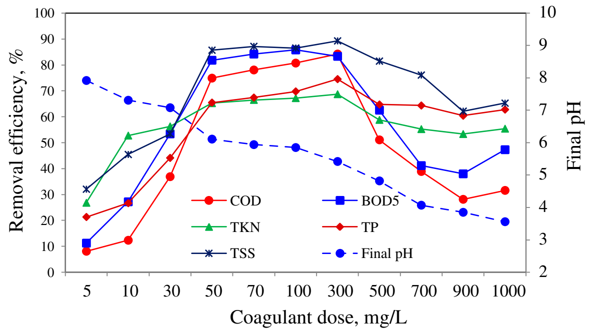

Fig. 3. Effect of coagulant dose on pollutants removal from real dairy wastewater (initial pH 8.0).

The increase in pollutants removal efficiency is due to increase in concentration of various hydrolysis species of coagulant which destabilize the colloidal particles. In addition, as it can be seen, maximum removal efficiency for most of the pollutants in real dairy wastewater achieved at coagulant dose equal 300 mg/L. Nevertheless, more increase of PACl reduces removal efficiency due to restabilization of colloidal suspension. In fact, with further increasing of coagulant dose up to 700–900 mg/L, final pH of dairy wastewater decreased to 3.85 (lower than isoelectric point equal 4.2) and pollutants removal efficiency decreased to minimum value PACl dose 900 mg/L. Since at dose 900 mg/L, final pH of solution is lower than isoelectric point (pH 4.2), hence, charge reversal of milk proteins caused decrease in pollutants removal. With an increase in PACl dose from 900 to 1,000 mg/L, final pH of solution decreased to 3.56; however, pollutants removal efficiency again increased. Formation of large amount of hydroxide flocs is responsible for pollutants removal by sweep coagulation at these higher dosages. It is known that the presence of milk proteins and other components in dairy wastewater keeps the pH constant, whereas, removal of these components decreases the pH.

Furthermore, Fig. 3 shows that the TSS removal and COD and BOD_5 reduction trends are similar to each other. This may be due to the high organic contents of the suspended solid particles. Similar findings were reported by Kushwaha et al. [1] for treatment of dairy wastewater by inorganic coagulants.

In concurrence with the results of this study (Fig. 3), it can be concluded that although the removal efficiency of most pollutants from real dairy wastewater are high, the concentration of pollutants in effluent of chemical coagulation process does not meet the effluent discharge standards to the environment. Thus, the effluent from conventional coagulation should be preceded by another treatment process to be completed. For this purpose, in this work, adsorption method was employed as a completion of treatment process to obtain discharge standards.

3.3. *Adsorption process on modified dried activated sludge*

Adsorption is a natural process by which molecules of dissolved compound collect on and adhere to the surface of an adsorbent solid. Adsorption occurs when the attractive forces at the carbon surface overcome the attractive forces of the liquid. Removal of organic compounds has been observed using activated carbon, activated alumina, and activated bauxite as adsorbents [31], and it is one of the most common technologies in treatment of different water resources or wastewaters which has been frequently used to remove organic pollutants [32]. At present work, an adsorption study with modified dried activated sludge was done on filtered wastewater after coagulation process (with coagulant dose = 300 mg/L at initial pH equal 8.0) to optimize pH, dosage, and contact time of adsorbent.

3.3.1. *Effect of initial pH*

It is well known that pH of the solution can affect the surface charge of the adsorbent, the degree of ionization of the different pollutants, the dissociation of functional groups on the active sites of the adsorbent. Consequently, the pH value of the aqueous solution is a significant controlling parameter in the process of adsorption. To study the effect of solution pH on the adsorption efficiency of modified dried activated sludge for pollutants removal from real dairy wastewater, experiments were carried out using various initial pHs varying from 2 to 12, at adsorbent dose of 5 g/L, and contact time of 60 min. As shown in Fig. 4, the adsorption was highly dependent on the pH of the solution and highest removal efficiency for most of pollutants were obtained at initial pH 6.0. The colloidal nature of dairy effluent is mostly due to the casein (milk protein). Dairy effluent has the isoelectric point (pHiso) around 4.2. The milk proteins contained in the dairy effluent are negatively charged at pH > pHiso and presumably get removed by the positive charged of chemically pretreated activated sludge [1,30].

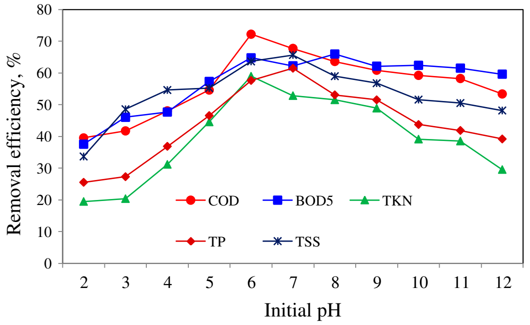

Fig. 4. Effect of initial pH on pollutants removal from real dairy wastewater by modified dried activated sludge ($T = 298$ K, adsorbent dose = 5 g/L, contact time = 60 min).

3.3.2. *Effect of adsorbent dosage*

The adsorbent dosage is a critical parameter because this determines the capacity of the adsorbent removal of pollutants. Therefore, to evaluate the effect of adsorbent dose on the adsorption of pollutants, 0.5 to 25 g/L modified dried activated sludge as adsorbent were used for adsorption experiments at fixed initial pH 6, and temperature 25°C for 60 min. As it can be seen from Fig. 5, the uptake of the pollutants increased quickly with increasing of adsorbent dose from 0.5 to 7–8 g/L and remained almost unchanged thereafter. This result can be explained by the fact that the sorption sites remain unsaturated during the sorption whereas the number of sites available for sorption site increases by increasing the adsorbent dose. A maximum of 79.04, 67.51, 66.78, 75.72, and 48.2% removal of the COD, BOD_5, TP, TSS, and turbidity were observed at adsorbent concentration of 7 g/L. Maximum removal efficiency equal 88.71% observed for TKN at adsorbent dose 6 g/L. Reduction of COD using adsorption on activated carbons has been reported by some researchers [23]. Moreover, Patel and Vashi [33] reported similar trend about COD,

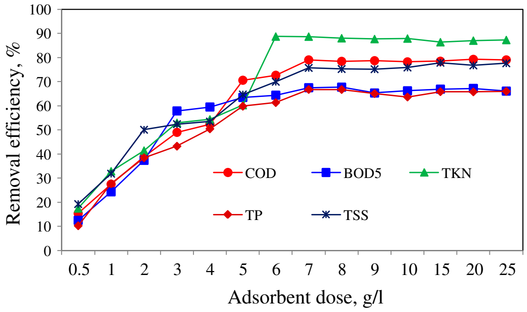

Fig. 5. Effect of adsorbent dose on pollutants removal from real dairy wastewater ($T = 298$ K, pH 6, contact time = 60 min).

BOD$_5$, and color removal from textile wastewater by adsorption process. In another study which was performed by Gandhimathi et al. [34], for the alum pretreated stabilized leachate, the maximum COD removal equal 28% using fly ash adsorbent with equilibrium time of 210 min and optimum dose of 6 g/L was achieved.

Furthermore, as it can be seen from Fig. 5, there was a non-significant increase in the percentage removal of pollutants when the adsorbent dose increases beyond the 7 g/L. This suggests that after a certain dose of adsorbent, the maximum adsorption is attained and hence the amount of pollutants remains constant even with further addition of dose of adsorbent [35–40]. On the other hand, this is due to the fact that for adsorbent dose more than optimum dose, the removal efficiency depends more upon the concentration of the solution and depends less upon the adsorbent dose. Consequently, in order to continue the adsorption studies, the adsorbent dose was fixed at 7 g/L.

3.3.3. Effect of contact time

The contact time is one of the most important parameters for practical application. The removal efficiency of pollutants adsorbed onto the modified dried activated sludge is shown as a function of time (15–240 min) in Fig. 6. The percent removal of pollutants onto the modified dried activated sludge significantly increases during the initial adsorption stage and then continues to increase at a relatively slow speed with contact time until a state of equilibrium is attained after about 90 min. The rapid adsorption of pollutants is probably due to the abundant availability of active sites on the sorbent surface during the first 45 min, so 48.67–82.18% removal efficiency attained after only 45 min for all pollutants. In addition, the maximum removal efficiency (approximately 58–90%) for various pollutants was obtained at contact time 90 min. Similar findings were reported by Patel and Vashi [33] about COD, BOD$_5$, and color removal from textile wastewater by adsorption process. Furthermore, COD removal efficiency equal 62.4% during 60 min were reported by Ademiluyi et al. [41] by adsorption process using granular AC (obtained from Nigerian bamboo) from refinery wastewater. Generally the removal rate of pollutants is rapid in the beginning, but it gradually decreases with time until it reaches equilibrium. This trend is attributed to the fact that a large number of vacant surface sites are existing for adsorption at the initial stage and, after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Similar finding was reported by other researchers [22,36,37].

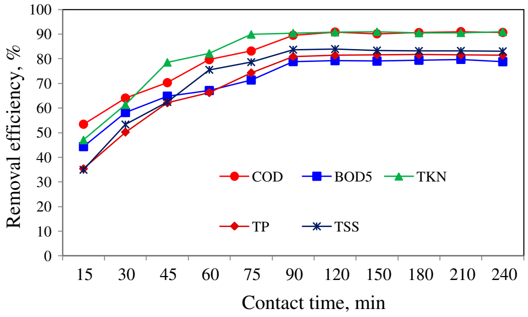

Fig. 6. Effect of contact time on pollutants removal from real dairy wastewater by modified dried activated sludge ($T = 298$ K, pH 6, adsorbent dose = 7 g/L).

3.3.4. Effect of temperature and thermodynamic studies

Temperature has an obvious effect on the adsorption capacity of the adsorbents. To understand the effect of temperature on the removal of common pollutants in real dairy wastewater by modified dried activated sludge, experiments were carried out at different temperatures ranging 293–318 K at pH 6 and adsorbent dosage 7 g/L. As it can be seen from Fig. 7, the removal efficiency of pollutants increased slightly, when the temperature was increased from 298 to 318 K. Adsorption is generally an exothermic process. Nevertheless, if the adsorption process is controlled by the diffusion process (intraparticle transport pore diffusion), the adsorption capacity will show an increase with an increase in temperature. This is fundamentally due to the fact that the diffusion is an endothermic process [42].

In fact, with an increase in temperature, the mobility of the dairy wastewater components increases and the retarding forces acting on the diffusing components decrease, thereby increasing the

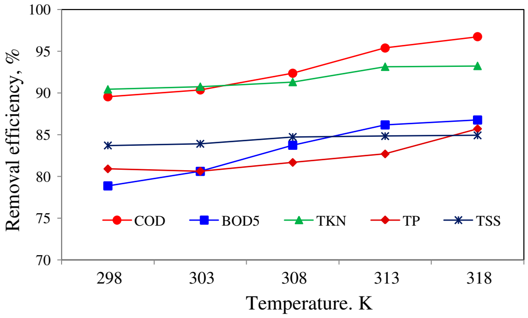

Fig. 7. Effect of temperature on pollutants removal from real dairy wastewater by modified dried activated sludge (pH 6, adsorbent dose = 7 g/L, contact time = 90 min).

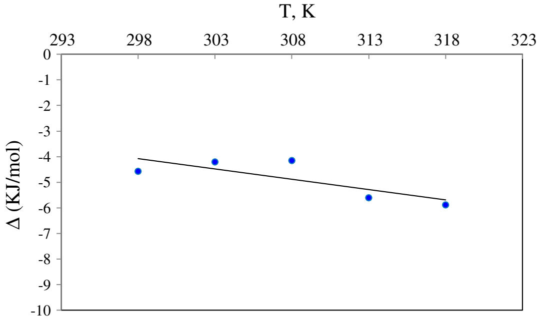

Fig. 8. Plot of Gibbs free energy change, ΔG°, vs. temperature, T.

adsorptive capacity of adsorbent. Similar findings were reported by Khodaie et al. [43], Bazrafshan et al. [9], and Bazrafshan et al. [36]. Furthermore, Patel and Vashi [33] surveyed the effect of temperature on the COD, BOD_5, and color removal from textile wastewater at different temperatures ranging 300 to 360 K. Their findings showed that the percentage of removal continuously increases as temperature increases. In addition, higher adsorption efficiency of COD from coking wastewater onto AC with an increase in temperature was reported by Zhang et al. [44].

Thermodynamic considerations of an adsorption process are required to conclude whether the process is spontaneous or not. Gibb's free energy change, ΔG°, is the fundamental measure of spontaneity. Reactions are spontaneously at a given temperature if ΔG° is a negative value. The thermodynamic parameters of Gibb's free energy change, ΔG°, enthalpy change, ΔH°, and entropy change, ΔS°, for the adsorption processes are calculated using the following equations: (Fig. 8)

$$\Delta G^{\circ} = -RT \ln K_a \quad (3)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (4)$$

where R is universal gas constant (8.314 J/mol/K) and T is the absolute temperature in K.

The thermodynamic parameter, Gibb's free energy change, ΔG°, is calculated using K_a obtained from Freundlich Eq. (7) and shown in Table 3. The negative values of ΔG° confirm the feasibility of the process and also the spontaneous nature of adsorption process with a high preference of pollutants (COD) by modified dried activated sludge. In addition, the decrease in the negative value of ΔG° with an increase in temperature indicates that the adsorption process of COD on adsorbent becomes more favorable at higher temperatures [45].

The enthalpy change, ΔH°, and the entropy change, ΔS°, for the adsorption process were obtained from the intercept and slope of Eq. (4) and found to be 19.9 kJ/mol and 0.08 kJ/mol/K, for the removal of COD. Adsorption process can be classified as physical adsorption and chemisorption by the magnitude of the enthalpy change. It is accepted that if magnitude of enthalpy change is less 84 kJ/mol, adsorption is physical. Nevertheless, chemisorption takes place in a range from 84 to 420 kJ/mol [46]. Consequently, the magnitude of enthalpy change indicates that the adsorption process is physical in nature.

The positive value of ΔH° indicates that the adsorption process is endothermic. Entropy has been defined as the degree of chaos of a system. Furthermore, the positive value of ΔS° suggests that some structural changes occur on the adsorbent and the

Table 3
Thermodynamics parameters for COD adsorption onto modified dried activated sludge

Temperature, K	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol/K)
298	−4.57	19.9	0.08
303	−4.21		
308	−4.15		
313	−5.61		
318	−5.88		

randomness at the solid/liquid interface in the adsorption system increases during the adsorption process [47]. Finally, it can be concluded that according to the thermodynamic properties, ΔG°, ΔH°, and ΔS°, adsorption of COD onto modified dried activated sludge was spontaneous, endothermic, and feasible in the temperature range of 298–318 K.

3.3.5. Isotherms study

The equilibrium of sorption is one of the most significant physicochemical aspects for the evaluation of the sorption process as an operation unit. The correlation of the isotherm information with the theoretical or empirical equation is appropriated for practical operation. In this study, the conventional isotherms in water and wastewater including Langmuir and Freundlich isotherms have been analyzed for removal of COD as an important pollution index in dairy wastewaters.

The Langmuir isotherm model is valid for monolayer adsorption onto surface containing finite number of identical sorption sites which is presented by the following equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{5}$$

where q_e is the amount of metal adsorbed per specific amount of adsorbent (mg/g), C_e is equilibrium concentration of the solution (mg/L), and q_m is the maximum amount of pollutant (adsorbate) required to form a monolayer (mg/g). The Langmuir equation can be rearranged to linear form for the convenience of plotting and determining the Langmuir constants (K_L) and maximum monolayer adsorption capacity of adsorbent (q_m). The values of q_m and K_L can be determined from the linear plot of $1/q_e$ vs. $1/C_e$:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L}\frac{1}{C_e} \tag{6}$$

The Freundlich equation is purely empirical based on sorption on heterogeneous surface, which is commonly described by the following equation:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{7}$$

where K_f and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The Freundlich equilibrium constants evaluated from the intercept and the slope, respectively, of the linear plot of $\log q_e$ vs. $\log C_e$ based on experimental data. The Freundlich equation can be linearized in logarithmic form for the determination of the Freundlich constants as shown below:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{8}$$

Table 4
Isotherm parameters for adsorption of COD onto modified dried activated sludge at various temperatures

	298 K	303 K	308 K	313 K	318 K
Langmuir isotherm					
q_m (mg/g)	80.90	93.09	102.59	85.62	89.48
K_L (L/ mg)	0.019	0.016	0.017	0.036	0.041
R^2	0.897	0.906	0.882	0.846	0.845
Freundlich isotherm					
K_f	6.33	5.31	5.06	8.62	9.26
n	2.23	1.99	1.85	2.25	2.23
R^2	0.944	0.946	0.933	0.919	0.931

The isotherms based on the experimental data and the parameters obtained from nonlinear regression by two models are presented in Table 4. According to results of this table, the correlation coefficient of the Freundlich model was higher than Langmuir model, indicating that the Freundlich model is suitable for describing the adsorption equilibrium of COD onto modified dried activated sludge.

4. Conclusion

Dairy wastewater usually contains high concentrations of organic matter, solids, and nutrients, as well as some dissolved inorganic pollutants. Consequently, dairy wastewater deserves special attention since its levels of potential contaminants typically exceed those levels considered hazardous for domestic wastewater. In this study, the treatment of dairy industry wastewater by conventional chemical coagulation using PACl (at various pH and coagulant dosages) and adsorption process by modified dried activated sludge (with $ZnCl_2$) was investigated. Maximum removal efficiency of pollutants (BOD_5 and COD) by chemical coagulation process was achieved at initial pH 8 and coagulant dose 100 mg/L in 60 min. In addition, optimum conditions for adsorption process were found to be: initial pH 6, adsorbent dose of 7 g/L, and contact time 90 min. The biosorption equilibrium data well was fitted by the Freundlich adsorption isotherm. The magnitude of enthalpy change indicates that the adsorption is physical in nature. Additionally, according to the thermodynamic properties, ΔG°, ΔH°, and ΔS°, adsorption of COD onto modified dried activated sludge was spontaneous, endothermic, and feasible in the temperature range of 298–318 K.

Acknowledgments

This study was funded by the health research deputy of Zahedan University of Medical Sciences (Project no: 5915) and was conducted in the Chemical Laboratory of School of Public Health, Zahedan University of Medical Sciences.

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