Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.21952

109 (2018) 152–161
March

Treatment of landfill leachate by hybrid coagulation and adsorption on modified waste activated sludge

Davoud Balarak[a], Edris Bazrafshan[b,*], Hossein Moein[a], Shima Nakhaei[a], Reza Badali[a], Hossein Kamani[a], Amir Hossein Mahvi[c], Nayyereh Poormollae[d]

[a]*Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, Iran, emails: dbalarak2@gmail.com (D. Balarak), ed_bazrafshan@yahoo.com (H. Moein), shimanakhaie@yahoo.com (S. Nakhaei), rbadali01@gmail.com (R. Badali), hossein_kamani@yahoo.com (H. Kamani)*
[b]*Health Sciences Research Center, Torbat Heydariyeh University of Medical Sciences, Torbat Heydariyeh, Iran, Tel. +98 9153411120; email: ed_bazrafshan@yahoo.com*
[c]*Department of Environmental Health, Graduate School of Public Health, Tehran University of Medical Sciences, Tehran, Iran, email: ahmahvi@yahoo.com*
[d]*Institute of Environment Protection of Sistan and Baluchestan Province, Zahedan, Iran, email: npoormollae@yahoo.com*

Received 22 August 2017; Accepted 26 January 2018

ABSTRACT

Currently, the production, treatment and management of landfill leachate are recognized as one of the greatest problems related to environmental and economical operation of sanitary landfills. Hence, in the current research, leachate treatment was studied using hybrid chemical coagulation using poly-aluminum chloride (PACl)-adsorption process using modified waste activated sludge (MWAS). The samples of leachate were collected from landfill site of Zahedan, Sistan and Baluchestan province, Iran. In the optimum conditions of coagulation process (pH = 8 and 400 mg/L PACl), the average 5-d biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), total phosphorus (TP), and total suspended solids (TSS) removals were approximately 67.5%, 69.3%, 63.6%, 73.1%, and 81.3%, respectively. Afterwards, the adsorption process on MWAS was applied for further treatment of the landfill leachate. Results illustrated a good performance for the adsorptive removal of major parameters including BOD_5, COD, TKN, TP, and TSS at initial pH of 8 and adsorbent dose of 12 g/L for contact time of 120 min. The adsorption data were in good agreement with Langmuir and Freundlich isotherms. The adsorption capacity calculated from the Langmuir isotherm was 103.09 mg COD/g of MWAS (at 308 K). Thermodynamic study of the adsorption process for the leachate treatment by MWAS showed the spontaneous nature of adsorption. Furthermore, based on the enthalpy magnitude, the process was found to be endothermic physisorption. Finally, the findings demonstrated the applicability of MWAS in the adsorptive leachate treatment.

Keywords: Landfill leachate; Chemical coagulation; Adsorption; Waste activated sludge

1. Introduction

In the past decades, the technical, demographic, and economic development of society has led to rise in the production of municipal solid wastes, which subsequently produces a disposal challenge [1]. One of the most embraced solid waste management practices worldwide, such as landfilling, recycling, composting and incineration, sanitary landfilling is definitely the most abundant approach in both developed and developing countries having to its easiness and monetary benefits [2]. Landfill leachate production is an unavoidable consequence of the landfilling process of municipal solid

* Corresponding author.

waste [3]. Landfill leachate commonly refers to the soluble matters exhausted from solid wastes dumped in the landfill sites after their contact with percolated rainfall water, surface runoff, underground water infiltration, and the activity of microorganisms in the garbage [4,5].

The complex quality of landfill leachate is a consequence of the diverse nature of the solid waste deposited in the landfill. Typically, leachate of landfill is identified as a dark-colored fluid which can contain high concentrations of organic matter, ammoniacal nitrogen, inorganic ions (such as chlorides), heavy metals, and various xenobiotic contaminants [6,7]. Various types of present compounds in landfill leachate can be toxic and even carcinogenic for humans. In addition, landfill leachates contain recalcitrant to biological process constituents which cannot be completely and successfully treated with biological processes. All these contaminants make the treatment of leachates complex and expensive; consequently, numerous combinations of physicochemical processes have been used for effective treatment [1,8–10]. In addition, with considering the challenges of biological systems, processes which can offer higher efficiency or be incorporated in standard processes (to reduce their shortcomings and improve their efficiency) are required. Currently, a large number of processes are available with a different nature, such as physical, chemical, and biological landfill leachate treatments and their combinations [10].

The conventional physical/chemical techniques proposed for treatment of landfill leachate include electrochemical oxidation [11], adsorption with various adsorbents [5,12–15], reverse osmosis [16], Fenton [17,18], ion exchange with different resins [19], advanced oxidation processes [20,21], dissolved air flotation [22], and coagulation/flocculation [3,22,23]. In order to meet the strict quality requirements for the direct release of landfill leachate into the environment, it is generally believed that a combination of chemical (coagulation–flocculation, advanced oxidation processes), physical (adsorption, membrane filtration, air stripping), and biological steps should be used [24].

Coagulation–flocculation is a common physicochemical process as pre- or post-treatment for many wastewater and landfill leachate which is performed in combination with other treatments to increase the removal of bio-refractory constituents and undesirable compounds in landfill leachate such as heavy metals [3]. Indeed, coagulation–flocculation is a conventional process which adds inorganic metal salts, including aluminum sulfate, poly-aluminum chloride (PACl), ferrous sulfate, ferric chloride, and ferric chloro-sulfate to effective removal of suspended and colloidal pollutants [25]. After removal of suspended matters in pre-treatment, secondary treatment, and tertiary treatment should be applied to eliminate soluble leachate fractions.

Among various tertiary treatments, the adsorption process seems appropriate to remove organic matters from the aqueous solutions. This method has been shown to be a proper treatment considering its low cost, simplicity, and convenience. However, the high cost of some adsorbents and the large amount of wastewater generally restrict its use [26,14,15]. To decrease the preparation costs, a possible approach is to apply inexpensive materials for preparing activated carbon. Hence, to prevent the cumbersome preparation and costly modification, waste activated sludge generated in a municipal wastewater treatment plant was chosen as the low-cost waste in this research. First, sludge-derived biochar (adsorbent) has attracted significant attention because of its simple preparing steps and economical cost. In addition, waste activated sludge itself needs to be treated in an economically and environmentally tolerable manner, and it is now one of the most serious challenges fronting society today [27,28].

At present, Zahedan landfill located in Zahedan city, Sistan and Baluchestan province does not have a suitable leachate treatment system and the landfill leachate infiltration could contaminate groundwater resources. Therefore, an effective treatment system is required to treat the leachate before severely polluting the environment. With this background in mind, we aimed to study the hybrid processes conventional coagulation (using PACl as coagulant) and adsorption processes, using modified waste activated sludge (MWAS) for municipal solid waste leachate treatment to decrease the level of pollutants discharge into the environment with minimum adverse effects. These processes may improve the elimination of different pollutants in the leachate.

2. Materials and methods

2.1. Landfill site and sampling

All the raw leachate samples were collected from a landfill site (29° 23′ 25.1″ N, 61° 00′ 9.6″ E), located at 20 km northeast of Zahedan city, Sistan and Baluchestan province, Iran. In total, 12 samples were taken during 2 months (every week one sample). Samples were collected manually, filled in polyethylene bottles, immediately transported to the laboratory, and preserved at 4°C in a refrigerator based on the standard methods for the examination of water and wastewater. It was estimated that every day, these landfills received approximately 120 tons of municipal solid waste. Based on the standard methods, the characteristics of the samples were specified. A comparison was made between the major parameters and the Iranian environmental quality regulations to describe the risk of leachate on the environment. In addition, the leachate samples were pretreated via the plain sedimentation.

2.2. Chemical coagulation

In general, jar test is recognized as a common technique for the analysis and optimization of coagulation and flocculation. This test includes batch experiments, rapid mixing, slow mixing, and sedimentation. The test was performed on an apparatus (Phipps and Bird, Richmond, VA) to optimize the pH level and coagulant dose at a mean temperature of 22°C ± 2°C. A pre-settled leachate sample (2 L) was added to each jar. First, the pH was adjusted (range of 2–12) with sulfuric acid and sodium hydroxide (1 M) at a PACl dose of 70 mg/L (before coagulant addition based on previous studies). Then, the PACl in various doses (5–1,000 mg/L) was added into each of the jars.

The processes of rapid and slow mixing were performed at a speed rate of 120 ± 5 rpm for 3 min and then at 20 ± 2 rpm during 20 min. Also, the settling time was 60 min for sedimentation of flocs driven from the coagulation–flocculation

process. The parameters were selected with respect to the conventional chemical coagulation. Following sedimentation, the supernatant was taken from 2 cm below the liquid surface. Finally, the supernatants were examined to identify chemical oxygen demand (COD), 5-d biochemical oxygen demand (BOD_5), total suspended solids (TSS), total Kjeldahl nitrogen (TKN), and total phosphorus (TP). The removal efficiency equation was used to describe the pollutant removal percentage:

$$\text{Removal efficiency, \%} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

where C_i and C_e denote the initial concentration and the effluent concentration of the mentioned parameters (mg/L), respectively.

2.3. Adsorption process

Following the chemical coagulation, in order to identify the optimal setting, we used the supernatant for the analysis of adsorption with MWAS.

2.3.1. Adsorbent preparation

The waste activated sludge samples were gathered from a municipal sewage treatment plant in Zahedan city, Sistan and Baluchestan province, Iran; their characteristics are presented in Table 1. The samples were dried at a temperature of 105°C in a hot oven for 1 d. To chemically activate the adsorbent, the dried powder waste activated sludge samples were soaked for 24 h in 1 M HCl at 1:1 (w/v ratio) at the room temperature. Afterwards, they were decanted and dried in a muffle furnace for 60 min at a temperature of 300°C. Distilled water was used several times to rinse the chemically pretreated waste activated sludge until pH turned neutral. The adsorbent was washed and dried at 105°C for 1 d. Finally, the prepared adsorbent was powdered and sieved to a particle size of 180 mesh for additional studies. Furthermore, the pH of the zero point charge (pHpzc) was determined based on the method reported by Foo and Hameed [29]. The pHpzc value was 7.4 indicating the neutral nature of the prepared adsorbent.

2.3.2. Batch experiments

These experiments were performed in the batch mode as a function of pH (range, 3–13), adsorbent dose (5–20 g/L), contact time (15–210 min), and temperature (298–318 K). A certain quantity of the adsorbent was added to 2 L flasks containing pre-settled and coagulated leachate landfill leachate (1,000 mL), following the plain sedimentation and coagulation process. It was maintained in a shaker (with controlled temperature) at 140 rpm for 4 h. Then, the adsorbent was removed from the solution. For separation of adsorbent from solution at the end of the experiments, and maintain uniformity of tested samples, the filtration method was used. The supernatant was filtered through a 0.45 μm glass fiber filter (Whatman). Then, the solution was analyzed in terms of BOD_5, COD, TKN, TP, TSS, and pH.

First, the adsorption of major parameters including BOD_5, COD, TKN, TP, and TSS were evaluated within a pH range of 3–13 at the temperature of 298 K. The initial pH was modified with H_2SO_4 or NaOH solution (1 M). The adsorption analysis was performed by changing the adsorbent dose within a range of 5–20 g/L at optimal pH and temperature of 298 K. The quantity of the adsorbed pollutant, q_e (mg/g), was measured under various conditions:

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

In this equation, C_0 and C_e represent the liquid-phase concentrations of various parameters (BOD_5, COD, TKN, TP, and TSS) at baseline and equilibrium (mg/g), respectively, V denotes the solution volume (L), and M denotes the quantity of the adsorbent (g).

The influence of temperature on removal efficiency with the adsorption process was studied at 298, 303, 308, 313, and 318 K at an initial pH of 8 and adsorbent dose of 12 g/L. After 120 min, the adsorbent was removed from the solution (by filtration) and examined for residual BOD_5, COD, TKN, TP, and TSS.

2.4. Analysis

All of the used materials had an extra pure or analytical grade. By using conventional methods, COD, BOD_5, total solids (TS), TSS, TKN, conductivity, and pH were identified [19]. COD was analyzed with a COD reactor and a spectrophotometer (DR 5000, HACH, USA). In addition, the BOD_5 was specified through the manometric technique with a Respirometric OxiTop® measuring system. TKN was examined through the Kjeldahl method. Moreover, a pH meter (UB-10, UltraBasic, USA) was used to measure pH and a conductivity meter was employed to analyze electrical conductivity. The dosage of heavy metals was measured using the atomic absorption spectrophotometer technique (Shimadzu AA-7000, Japan) after acid digestion.

Table 1
Composition of sludge used for preparation of adsorbent

Parameters	Characteristics
Sludge type	Return line
pH	7.4–7.6
Total suspended solids, g/L	2.9
Settleable solids after 30 min, mL/L	327
Sludge age, d	12

3. Results and discussion

3.1. Leachate characterization

Various parameters, including the waste composition, elapsed time, temperature, landfilling depth, and site hydrology, can affect the quality and quantity of leachate [30,31]. As a result, the quality of leachate is related to its site, and treatment techniques vary in different climatic and operational conditions.

Table 2
Characteristics of the landfill leachate

Parameters	Raw leachate, mean ± SD	Pre-settled leachate, mean ± SD	Permitted levels in Iran
Total COD (mg/L)	3,503 ± 267	3,467 ± 254	60
Total BOD_5 (mg/L)	1,538 ± 102	1,507 ± 137	30
BOD_5/COD	0.44	0.43	–
TS (mg/L)	4,831 ± 162	4,217 ± 103	–
TSS (mg/L)	1,846 ± 326	1,512 ± 102	60
TKN (mg/L)	123.6 ± 15.3	123.5 ± 12.1	2.5
TP (mg/L)	15.7 ± 3.2	15.6 ± 2.6	6
Turbidity (NTU)	764 ± 57	693 ± 37	50
Conductivity (mS/cm)	13.7 ± 1.1	13.81 ± 1.3	–
pH	7.61 ± 0.52	7.63 ± 0.24	6.5–8.5
Cadmium (mg/L)	0.44 ± 0.21	0.44 ± 0.21	0.1
Chromium (IV) (mg/L)	0.29 ± 0.18	0.28 ± 0.15	0.5
Lead (mg/L)	0.04 ± 0.07	0.04 ± 0.07	1.0
Nickel (mg/L)	0.03 ± 0.04	0.03 ± 0.04	2.0
Zinc (mg/L)	0.54 ± 0.04	0.54 ± 0.04	2.0

Table 2 presents the composition of raw and pre-settled leachate after 4 h of settling, as well as the Iranian guidelines for discharge in the urban sewage system. Most of the parameters' values were reduced after 4 h of preliminary settling time. However, based on the comparison of these values, levels of COD, BOD_5, TSS, TKN, and cadmium were quite higher than the standards suggested in Iran (Table 2). The main characteristics of pre-settled leachate were as follows: COD, 3,467 ± 254; BOD_5, 1,507 ± 1 37; and TKN, 127.5 ± 12.1 mg/L. Considering the high BOD_5 and COD values, heavy contamination with organic matters was reported. Therefore, the leachate had to be treated prior to discharge into environment. Moreover, BOD_5/COD ratio was measured as a marker of biodegradability; in other words, higher BOD_5/COD ratio represents greater wastewater biodegradability. In the present study, the BOD_5/COD ratio was 0.43–0.44 in raw leachate, representing its biodegradability; however, the biodegradability was not very high. In the literature, high BOD_5/COD ratio (range, 0.56–0.62) has been reported in the leachate from municipal solid waste incineration plants [32].

Heavy metals are dangerous components, commonly found in leachate. In the present study, metals in the landfill leachate had fairly low concentrations (Table 2). However, the cadmium concentration in raw leachate exceeded the permissive levels. According to a review from the US EPA, the mean concentrations of heavy metals in landfill leachate were as follows: cadmium, 0–17 mg/L; chromium, 0–33 mg/L; lead, 0–12 mg/L; mercury, 0–0.2 mg/L; nickel, 0–9 mg/L; and zinc, 0–1,000 mg/L [33]. Metal solubilization from solid waste was identified by pH variations, considering the organic acid generation, which has a direct relation with the landfill, age [34].

Preliminary settling is a common technique, which does not require any chemical additions. Despite the fact that some researchers have noted the significance of natural settling, little evidence is available on the impact of preliminary settling time on pollutant removal; apparently, leachate with such quality should not be released in the environment.

In the current research, the raw landfill leachate was left to remain in a tank prior to adding PACl as the coagulant. The settling time influenced the removal of COD, BOD_5, TS, TSS, and turbidity within the first 4 h. According to Table 2, TS and TSS reduced, respectively, from 4,831 to 4,217 and from 1,846 to 1,512 mg/L (removal efficiency ~12% to 18%). Furthermore, total COD and BOD_5 were reduced in the landfill leachate from 3,503 and 1,538 mg/L to 3,467 and 1,507 mg/L, respectively (removal efficiency ~1% to 2%). Additionally, BOD_5/COD ratio was remained unchanged (0.43–0.44).

3.2. Effect of the coagulation process

Coagulation is recognized as one of the main stages in water and wastewater treatment. The colloidal particles are grown through destabilizing suspended particles and floc formation via adsorption and aggregation [35]. On the other hand, the coagulation/flocculation stage is necessary for decreasing the TSS, organic content, and color with the purpose of promoting treatment efficiency. In our study, chemical coagulation was used as the adsorption pretreatment. Reduction of pollutants loading in post-treatment was the main objective of chemical coagulation. On the other hand, to obtain dischargeable effluents, PACl was selected as the major coagulant. Hence, PACl as coagulant was added to samples (pre-settled leachate) for effective removal of organic substances and impurities (including TS, TSS, TKN, and heavy metals).

3.2.1. Effect of initial pH of solution on coagulation process

The removal of pollutants from aqueous environments by coagulation and similar processes is majorly affected by the solution pH [36]. To identify the impact of pH on leachate treatment efficiency, pH values were adjusted as 3–13 and maintained by continuously adding sulfuric acid or sodium hydroxide. According to Fig. 1, maximum removal efficiency

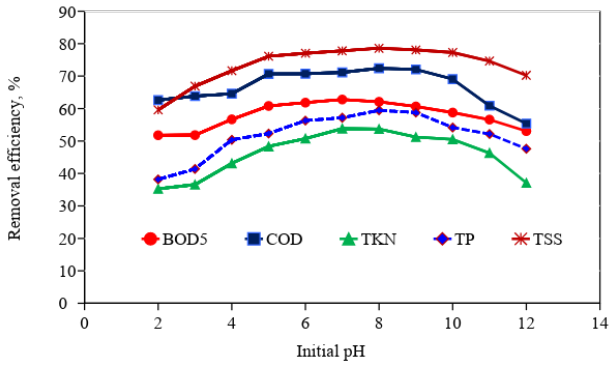

Fig. 1. Effect of initial pH on BOD_5, COD, TKN, TP, and TSS removal from pre-settled landfill leachate (PACl dose = 70 mg/L).

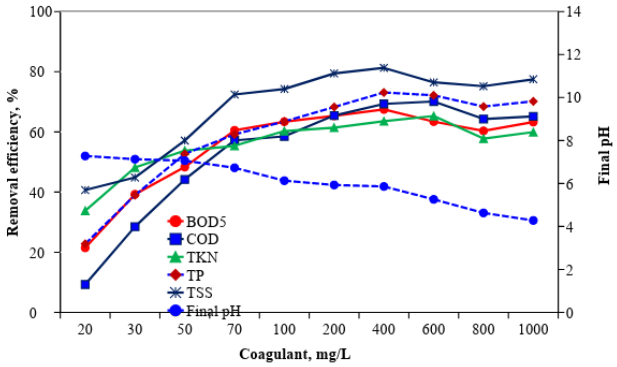

Fig. 2. Effect of coagulant dose on BOD_5, COD, TKN, TP, and TSS removal from landfill leachate (initial pH = 8.0).

for all parameters in coagulated leachate was achieved at pH 8.0 (62.09%, 72.43%, 53.68%, 59.46%, and 78.58% for BOD_5, COD, TKN, TP, and TSS, respectively).

For pH values above 8, Al(III) speciation showed that aluminum ions in water are in form of $Al(OH)_4$ ions. Removal efficiency by PACl was reduced given the electrostatic repulsion between $Al(OH)_4$ ions and colloidal particles in the leachate which were negatively charged [37]. In this regard, Bazrafshan et al. [38] and Keen [8] have reported consistent findings on dairy wastewater treatment using inorganic coagulants [38,39]. Based on the findings, an initial pH of 8.0 was considered as optimal for further studies.

3.2.2. Influence of coagulant dose on treatment of pre-settled leachate

The coagulation process efficiency is strongly influenced by the coagulant dose; consequently, PACl dose ranged from 20 to 1,000 mg/L to study the effect of this variable of treatment efficiency. The results of coagulation process on pre-settled leachate are presented in Fig. 2 at an optimal pH of 8. As presented in Fig. 2, minimum removal efficiency of 21.5%, 9.3%, 33.8%, 22.8%, and 40.7% was observed at lower PACl doses (20 mg/L); for BOD_5, COD, TKN, TP, and TSS, respectively. Increasing the dose of PACl coagulant consistently improved the BOD_5, COD, TKN, TP, and TSS removal efficiency achieving 65.4%, 69.3%, and 70.1% COD removal at a coagulant dose of 200, 400, and 600 mg/L, respectively. In addition, TSS removal efficiency of 79.4%, 81.2%, and 76.5% were achieved at coagulant dose of 200, 400, and 600 mg/L, respectively. Similar trends were observed for other parameters.

Another point to consider is that a further increase in PACl coagulant dose did not yield significant changes in most of studied parameters. Even in some cases, higher PACl doses (800–1,000 mg/L) did decrease the COD and other parameters removal efficiency. For example, removal efficiency for COD and BOD_5 was reduced from 69.3% and 67.3% at coagulant dose of 400 mg/L to 65.1% and 63.3% at coagulant dose 1,000 mg/L. This phenomenon could result from re-stabilization of colloidal particles triggered by the increasing of coagulant dose [40]. Hence, due to high removal efficiency which was achieved at coagulant dose 400 mg/L and economic considerations, this dose was selected for further experiments. Also, as shown in Fig. 2, PACl addition to pre-settled landfill leachate reduced the final pH; the highest rate of reduction was reported at a coagulant dose of 1,000 mg/L (final pH, 4.28). Similar findings were reported by Oloibiri et al. [7] on application of coagulation process using PACl as pretreatment on stabilized landfill leachate.

According to the findings of current study, although the elimination of the most parameters from leachate was high, the pollutants concentrations in the chemical coagulation effluent were not in accordance with the effluent discharge standards. The concentration of major parameters including BOD_5, COD, TSS, TKN, and TP after chemical coagulation at PACl dose 400 mg/L reached 490.37, 1,064.02, 283.05, 45.003, and 4.19 mg/L, respectively. Hence, the effluent from the standard coagulation process should undergo any additional treatment process. Consequently, in this study, the adsorption on MWAS was used to improve the treatment process and find the standards.

3.3. Leachate treatment using the adsorption process on MWAS

Among various tertiary treatments, the adsorption seems appropriate to remove organic elements from wastewater. Adsorption involves the adherence of dissolved compound molecules to the adsorbent solid surface. The activated carbon is normally used as an adsorbent in wastewater treatment. However, several researchers have used some inexpensive adsorbents for wastewater treatment [12,14,15,41,42]. In the current study, the adsorption process with MWAS was performed on pre-coagulated leachate, following coagulation (coagulant dose, 400 mg/L; initial pH, 8.0) with the purpose of optimizing pH, adsorbent dose, contact time, and temperature.

3.3.1. Influence of initial pH on pre-coagulated leachate treatment using MWAS in adsorption process

Evidently, adsorbent surface charge, pollutant ionization, and dissociation of functional groups on active adsorbent sites are influenced by pH [15,43,44]. Therefore, pH is a key factor in controlling adsorption. In order to evaluate the effectiveness of the pH on the adsorption efficiency of MWAS for leachate treatment, different initial pH values (range, 3–13) were used at an adsorbent dose of 8 g/L and contact time of 120 min (based on the number of pre-tests).

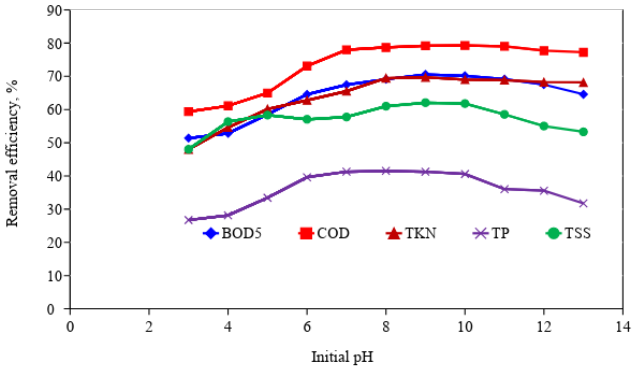

Fig. 3. Effect of initial pH on adsorption of BOD_5, COD, TKN, TP, and TSS from pre-coagulated leachate using MWAS (T = 298 K; adsorbent dose = 8 g/L; contact time = 120 min).

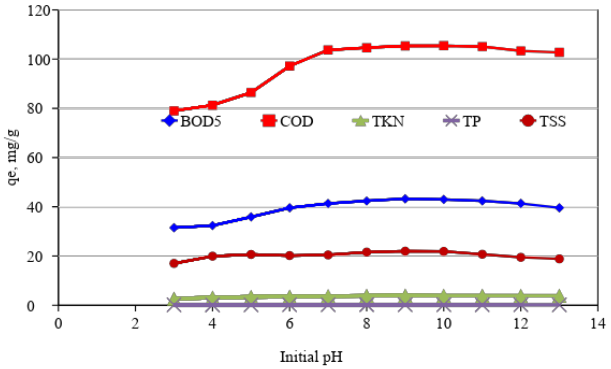

Fig. 4. Effect of pH on BOD_5, COD, TKN, TP, and TSS removal from pre-coagulated landfill leachate (T = 298 K; adsorbent dose = 8 g/L; contact time = 120 min).

According to Fig. 3, the removal efficiency increased from 51.39%, 59.38%, 47.98%, 26.73%, and 48.03% (initial pH = 3) with increasing initial pH and reached 69.13%, 78.68%, 69.45%, 41.53%, and 61.01% in the initial pH of 8 for BOD_5, COD, TKN, TP, and TSS, respectively. Removal of all parameters reduced beyond a pH of 8.0. Similar trends were observed for uptake of pollutants from landfill leachate (Fig. 4). Bazrafshan et al. [38] reported similar results on the adsorption of mentioned parameters by modified dried activated sludge in treatment of dairy wastewater MWAS. In addition, similar trend was reported by Ramya et al. [45] on COD reduction from coffee processing wastewater by adsorption process using agricultural wastes. As a result, an initial pH of 8.0 was considered to be optimal value for further evaluations [45].

3.3.2. Influence of adsorbent dose on treatment of pre-coagulated leachate by the adsorption process

Evidently, the rise in adsorbent dosage increased the pollutants adsorption, considering the higher accessibility of exchangeable regions or the surface area; however, it reduced the adsorption quantity, thereby diminishing the effective surface area for adsorption [12,15,46]. The effect of adsorbent dose on adsorption in landfill leachate is presented in Fig. 5. As presented in this figure, the removal efficiency increased with the increase of adsorbent dose. The removal efficiency of BOD_5, COD, TKN, TP, and TSS increased from 33.19%, 34.95%, 36.6%, 22.91%, and 26.47% to 77.07%, 85.23%, 77.73%, 44.63%, and 66.78%, respectively, by raising the adsorbent dose from 5 to 12 g/L. Changes in removal efficiency for all parameters with more increase in the adsorbent dose (after 12 g/L), was not very effective and significant. Hence, adsorbent dose 12 g/L was selected as the optimal dose for further experiments.

In addition as shown in Fig. 5, the adsorption capacity reduced by raising the adsorbent dose. Obviously, by increasing the quantity of adsorbent, the adsorption efficiency improved, while the adsorption capacity decreased with the adsorbed amount per unit mass. Based on the findings, the number of accessible adsorption regions enhances through increasing the adsorbent dose and promotes the removal efficiency. The decline in the adsorption potential by raising the adsorbent dose is majorly attributed to the

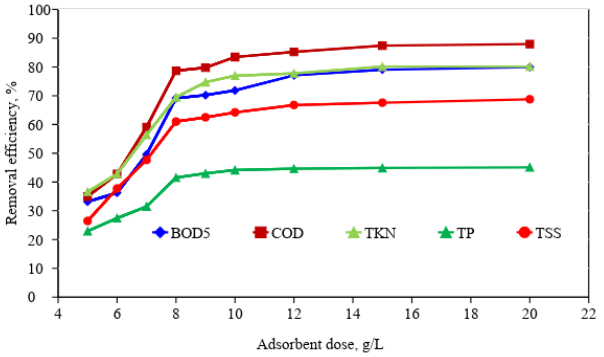

Fig. 5. Effect of adsorbent dose on the removal of BOD_5, COD, TKN, TP, and TSS from pre-coagulated landfill leachate (T = 298 K; pH = 8; contact time = 120 min).

unsaturation of adsorption sites via adsorption reactions. Particle interactions including aggregation might have also resulted from high adsorbent dosage. This aggregation might decrease the adsorbent's total surface area and enhance the diffusional path length. In addition, the particle interactions might desorb some of the loosely attached adsorbate [47]; in this regard, similar results have been observed by other researchers [39,45,48].

An important physiochemical aspect in terms of the evaluation of sorption processes is the sorption equilibrium. Indeed, the isotherm provides a relation between the concentration of adsorbate (COD) in solution and the amount of adsorbate (COD) adsorbed on the solid phase when both phases are in equilibrium. Hence, in this research, in order to study the adsorption isotherm, two conventional equilibrium isotherms including Langmuir and Freundlich were analyzed.

Langmuir isotherm model is valid for monolayer adsorption onto surface containing fixed number of identical sorption sites. The linear saturated monolayer isotherm can be represented as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_l}\frac{1}{C_e} \tag{3}$$

where q_e is the amount of COD 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 COD required to form a monolayer (mg/g). The Langmuir constants (K_L) and maximum monolayer adsorption capacity of MWAS (q_m) can be determined from the linear plot of $1/q_e$ vs. $1/C_e$ [41–44].

The Freundlich equation is absolutely empirical based on sorption on heterogeneous surface, which is normally defined by the following equation (linear form):

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (4)$$

where K_f and $1/n$ are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively.

The isotherms based on the experimental data and the parameters obtained from nonlinear regression by two models are presented in Table 3. As presented in this table, the correlation coefficient of the Freundlich model was more than Langmuir model, indicating that the Freundlich model is suitable to describe the adsorption equilibrium of COD of landfill leachate onto MWAS.

3.3.3. Effect of contact time on pre-coagulated leachate treatment using the adsorption process by MWAS

The time of adsorbent–adsorbate contact is a major factor in determining the time of adsorption process at equilibrium. The time required to attain equilibrium was affected by the activated carbon features and accessible sorption sites. At present study, to study the effect of contact time on the adsorption process, batch adsorption experiments were carried out at different contact times (15–210 min). As presented in Fig. 6. the adsorption efficiency was improved by increasing the contact time. High removal efficiency was achieved within the first 60 min; equilibrium was attained within 120 min for all the parameters. Consequently, contact time of 120 min was selected as equilibrium time for more experiments. Pollutants (adsorbate) removal is usually fast initially, while it slows down until reaching equilibrium. The pollutant removal rate is higher at first, considering the greater surface of the available adsorbent for adsorption. Since these sites were exhausted, the uptake was managed by transport from exterior to interior regions [49]. Considering the fact that the active sorption sites are fixed and every active site is able to only adsorb one molecule inside a monolayer, the adsorbate uptake is fast initially, while it slows down as the competition for reduced available sites grows among pollutants.

3.3.4. Influence of temperature on the adsorption process by MWAS for pre-coagulated leachate treatment

The impact of temperature on the treatment of pre-coagulated leachate was evaluated with MWAS as the adsorbent. As it can be seen in Fig. 7, the adsorption efficiency was improved by raising the temperature from 298 to 318°K. The increase in removal efficiency has been relatively mild. However, an increase in the removal efficiency was observed with increasing temperature. For example removal efficiency

Table 3
Isotherm parameters for adsorption of COD in pre-coagulated leachate onto MWAS at various temperatures

	298 K	303 K	308 K	313 K	318 K
Langmuir isotherm					
q_m (mg/g)	80.65	93.46	103.09	85.47	89.29
K_L (L/mg)	0.018	0.015	0.015	0.033	0.037
R^2	0.8974	0.9068	0.8825	0.8460	0.8455
Freundlich isotherm					
K_f	6.33	5.31	5.06	8.62	9.54
N	2.23	1.99	1.85	2.25	2.23
R^2	0.9445	0.9464	0.9334	0.9192	0.9311

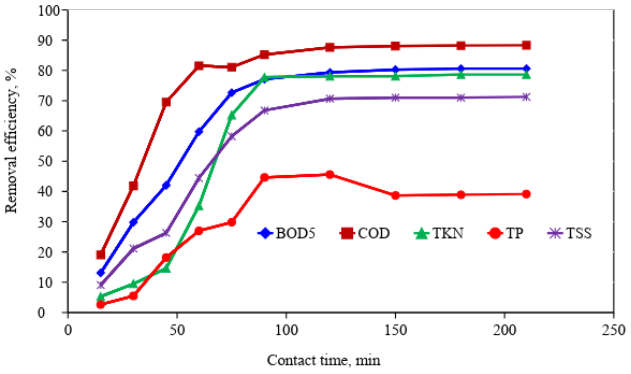

Fig. 6. Effect of contact time on BOD_5, COD, TKN, TP, and TSS removal from pre-coagulated leachate (T = 298 K; pH = 8; adsorbent dose = 12 g/L).

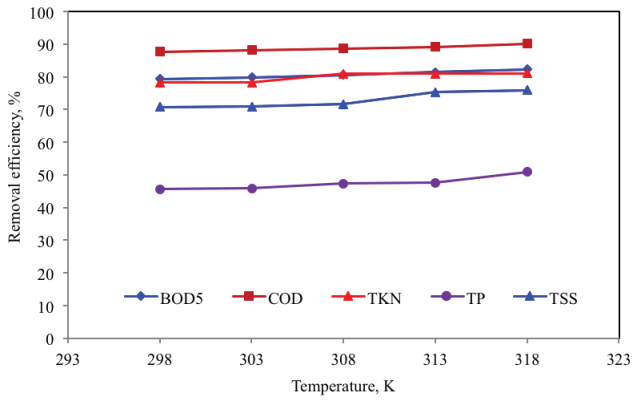

Fig. 7. Effect of temperature on BOD_5, COD, TKN, TP, and TSS removal from pre-coagulated leachate (contact time = 120 min; pH = 8; adsorbent dose = 12 g/L).

from 89.5% and 78.8% at 298°K reached 96.7% and 86.7% at 318°K, for COD and BOD_5, respectively. Therefore, we can conclude that this is an endothermic process with the greatest influence on the adsorption. The required energy is provided easier and improves the adsorption percentage by increasing the temperature. Furthermore, the increase in the adsorption efficiency due to raising the temperature might be associated with the enlarged pore size of adsorbent particles at higher

temperatures [50]. Following the equilibrium, the adsorption efficiency did not significantly improve; in this regard, other researchers have reported consistent results [44,51].

In the adsorption process, thermodynamic considerations are required to accomplish whether the process is spontaneous or not. Gibb's free energy change, $\Delta G°$, is the critical measure of spontaneity.

Reaction is spontaneously at a particular temperature if $\Delta G°$ is a negative value. The thermodynamic parameters of Gibb's free energy change, $\Delta G°$; enthalpy change, $\Delta H°$; and entropy change, $\Delta S°$, for processes of adsorption are calculated by Eqs. (5) and (6):

$$\Delta G^0 = -RT \ln K_a \quad (5)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (6)$$

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

The thermodynamic factor, Gibb's free energy change, $\Delta G°$, is calculated using K_a resulted from Freundlich isotherm model and is presented in Table 4.

As shown in Fig. 8, the plot of Gibb's free energy change, $\Delta G°$, against temperature, T, is linear. Furthermore, the enthalpy change, $\Delta H°$, and the entropy change, $\Delta S°$, for the process of the adsorption were achieved from the intercept and slope of Eq. (6) and found to be 19.9 kJ mol^{-1} and 0.08 kJ/mol/K, respectively. The negative values of $\Delta G°$ approve the feasibility of the adsorption process and also the spontaneous nature of adsorption with a high preference of COD by MWAS. In addition, the decrease in the negative value of $\Delta G°$ with an increase in the temperature indicates that the adsorption process of COD on MWAS becomes more favorable at higher temperatures [52–54].

Table 4
Thermodynamics parameters for COD adsorption on MWAS

Temperature, K	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/mol/K)
298	–4.57	19.9	0.08
303	–4.21		
308	–4.15		
313	–5.61		
323	–5.88		

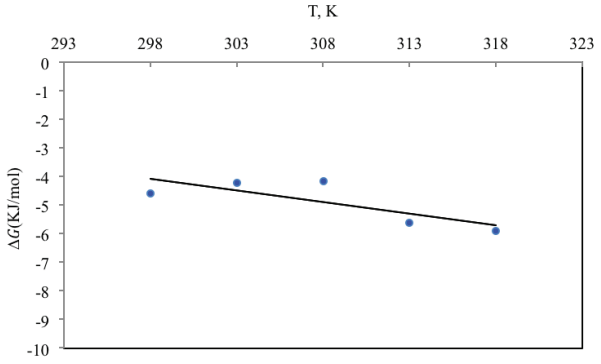

Fig. 8. Plot of Gibbs free energy change, $\Delta G°$, vs. temperature, T.

The adsorption process can be categorized as a physical adsorption and chemisorption by the amount of the enthalpy change. It was found that if the amount of enthalpy change is less than 84 kJ/mol, the adsorption is physical. Conversely, the chemisorption will take place in the range of 84 to 420 kJ/mol [52–54]. Based on the findings presented in Table 4, it can be concluded that the physisorption is much more favorable for the adsorption of COD of landfill leachate. Furthermore, the positive value of $\Delta H°$ shows that the adsorption reaction is endothermic. Entropy is defined as the degree of chaos of a system. The positive value of $\Delta S°$ recommends that some structural changes occur on the adsorbent and the randomness at the solid/liquid interface in the adsorption system increases during the adsorption process [52–54].

4. Conclusion

Inappropriate landfill management may pose serious environmental challenges through discharge of high strength polluted wastewater (leachate). In the present study, the treatment of landfill leachate by hybrid coagulation and adsorption on MWAS was investigated. The influence of the critical operating parameters such as the pH of solution and coagulant dose for coagulation and pH, contact time, adsorbent dose, and temperature on the adsorption process was investigated. The findings revealed acceptable performance of the combined coagulation and adsorption processes for the adsorptive removal of the major parameters including BOD_5, COD, TKN, TP, and TSS present in the landfill leachate at an initial pH of 8, adsorbent dose of 12 g/L, and the equilibrium time of 120 min. The treatment efficiency of leachate improved by an increase in the temperature of solution. In fact, the negative values of free-energy change confirmed the feasibility of the process and the spontaneous nature of adsorption. Furthermore, based on the enthalpy magnitude, the process was found to be endothermic physisorption. Finally, the findings demonstrated the applicability of MWAS for the effective treatment of landfill leachate.

Acknowledgment

The authors would like to express their gratitude to Zahedan University of Medical Sciences for the funding of this study (Project No. 6552).

References

[1] D.R. Ramírez-Sosa, E.R. Castillo-Borges, R.I. Méndez-Novelo, M.R. Sauri-Riancho, M. Barcelo-Quintal, J.M. Marrufo-Gomez, Determination of organic compounds in landfill leachates treated by Fenton-adsorption, Waste Manage., 33 (2013) 390–395.
[2] P. Mandal, B.K. Dubey, A.K. Gupta, Review on landfill leachate treatment by electrochemical oxidation: drawbacks, challenges and future scope, Waste Manage., 69 (2017) 250–273.
[3] Z.J. Yong, M.J. Bashir, C.A. Ng, S. Sethupathi, J.W. Lim, A sequential treatment of intermediate tropical landfill leachate using a sequencing batch reactor (SBR) and coagulation, J. Environ. Manage., 205 (2018) 244–252.

[4] E. Bou-Zeid, M. Ei-Fadel, Parametric sensitivity analysis of leachate transport simulations at landfills, Waste Manage., 24 (2004) 681–689.
[5] S. Lee, J. Hur, Heterogeneous adsorption behavior of landfill leachate on granular activated carbon revealed by fluorescence excitation emission matrix (EEM)-parallel factor analysis (PARAFAC), Chemosphere, 149 (2016) 41–48.
[6] T. Robinson, Removal of toxic metals during biological treatment of landfill leachates, Waste Manage., 63 (2017) 299–309.
[7] V. Oloibiri, I. Ufomba, M. Chys, W.T. Audenaert, K. Demeestere, S.W. Van Hulle, A comparative study on the efficiency of ozonation and coagulation–flocculation as pretreatment to activated carbon adsorption of biologically stabilized landfill leachate, Waste Manage., 43 (2015) 335–342.
[8] O.S. Keen, Characterisation of ultraviolet-absorbing recalcitrant organics in landfill leachate for treatment process optimization, Waste Manage. Res., 35 (2017) 325–328.
[9] J. Xu, Y. Long, D. Shen, H. Feng, T. Chen, Optimization of Fenton treatment process for degradation of refractory organics in pre-coagulated leachate membrane concentrates, J. Hazard. Mater., 323 (2017) 674–680.
[10] P. Amirian, E. Bazrafshan, A. Payandeh, Optimisation of chemical oxygen demand removal from landfill leachate by sonocatalytic degradation in the presence of cupric oxide nanoparticles, Waste Manage. Res., 35 (2017) 636–646.
[11] N. Huda, A.A. Raman, M.M. Bello, S. Ramesh, Electrocoagulation treatment of raw landfill leachate using iron-based electrodes: effects of process parameters and optimization, J. Environ. Manage., 204 (2017) 75–81.
[12] A.A. Halim, H.A. Aziz, M.A.M. Johari, K.S. Ariffin, Y.T. Hung, Removal of ammoniacal nitrogen and COD from semi-aerobic landfill leachate using low-cost activated carbon zeolite composite adsorbent, Int. J. Environ. Waste Manage., 4 (2009) 399–411.
[13] K. Peeters, G. Lespes, R. Milačič, J. Ščančar, Adsorption and degradation processes of tributyltin and trimethyltin in landfill leachates treated with iron nanoparticles, Environ. Res., 142 (2015) 511–521.
[14] M. Ye, M. Sun, X. Chen, Y. Feng, J. Wan, K. Liu, D. Tian, M. Liu, J. Wu, A.P. Schwab, X. Jiang, Feasibility of sulfate-calcined eggshells for removing pathogenic bacteria and antibiotic resistance genes from landfill leachates, Waste Manage., 63 (2017) 275–283.
[15] K.Y. Foo, B.H. Hameed, An overview of landfill leachate treatment via activated carbon adsorption process, J. Hazard. Mater., 171 (2009) 54–60.
[16] A. Chianese, R. Ranauro, N. Verdone, Treatment of landfill leachate by reverse osmosis, Water Res., 33 (1999) 647–652.
[17] J. Xu, Y. Long, D. Shen, H. Feng, T. Chen, Optimization of Fenton treatment process for degradation of refractory organics in pre-coagulated leachate membrane concentrates, J. Hazard. Mater., 323 (2017) 674–680.
[18] M.R. Sabour, A. Amiri, Comparative study of ANN and RSM for simultaneous optimization of multiple targets in Fenton treatment of landfill leachate, Waste Manage., 65 (2017) 54–62.
[19] M.J.K. Bashir, H.A. Aziz, M.S. Yusoff, S.Q. Aziz, S. Mohajeri, Stabilized sanitary landfill leachate treatment using anionic resin: treatment optimization by response surface methodology, J. Hazard. Mater., 128 (2010) 115–122.
[20] G. DelMoro, A. Mancini, G. Mascolo, C. Di Iaconi, Comparison of UV/H_2O_2 based AOP as an end treatment or integrated with biological degradation for treating landfill leachates, Chem. Eng. J., 218 (2013) 133–137.
[21] M. Chys, V.A. Oloibiri, W.T Audenaert, K. Demeestere, S.W. Van Hulle, Ozonation of biologically treated landfill leachate: efficiency and insights in organic conversions, Chem. Eng. J., 277 (2015) 104–111.
[22] M.N. Adlan, P. Palaniandy, H. Abdul Aziz, Optimization of coagulation and dissolved air flotation (DAF) treatment of semi-aerobic landfill leachate using response surface methodology (RSM), Desalination, 277 (2011) 74–82.
[23] F.J. Rivas, F. Beltran, F. Carvalho, B. Acedo, O. Gimeno, Stabilized leachate: sequential coagulation-flocculation - chemical oxidation process, J. Hazard. Mater., 116 (2004) 95–102.
[24] J. Gao, V. Oloibiri, M. Chys, W. Audenaert, B. Decostere, Y. He, H. Van Langenhove, K. Demeesteree, S.W.H. Van Hulle, The present status of landfill leachate treatment and its development trend from a technological point of view, Rev. Environ. Sci. Biotechnol., 14 (2015) 93–122.
[25] A.K. Verma, R.R. Dash, P. Bhunia, A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters, J. Environ. Manage., 93 (2012) 154–168.
[26] E. Bazrafshan, P. Amirian, A.H. Mahvi, A. Ansari-Moghaddam, Application of adsorption process for phenolic compounds removal from aqueous environments: a systematic review, Global NEST J., 18 (2016) 146–163.
[27] J. Wang, Z. Liao, J. Ifthikar, L. Shi, Y. Du, J. Zhu, S. Xi, Z. Chen, Z. Chen, Treatment of refractory contaminants by sludge-derived biochar/persulfate system via both adsorption and advanced oxidation process, Chemosphere, 185 (2017) 754–763.
[28] W. Zhang, J. Zheng, P. Zheng, R. Qiu, Atrazine immobilization on sludge derived biochar and the interactive influence of coexisting Pb(II) or Cr(VI) ions, Chemosphere, 134 (2015) 438–445.
[29] K. Foo, B. Hameed, Microwave-assisted preparation and adsorption performance of activated carbon from biodiesel industry solid reside: influence of operational parameters, Bioresour. Technol., 103 (2011) 398–404.
[30] A. Amiri, M.R. Sabour, Multi-response optimization of Fenton process for applicability assessment in landfill leachate treatment, Waste Manage., 34 (2014) 2528–2536.
[31] G. Tchobanoglous, F. Kreith, Handbook of Solid Waste Management, 2nd ed. McGraw-Hill, New York, USA, 2002.
[32] J. Ye, Y. Mu, X. Cheng, D. Sun, Treatment of fresh leachate with high strength organics and calcium from municipal solid waste incineration plant using UASB reactor, Bioresour. Technol., 102 (2011) 5498–5503.
[33] Z.L. Ye, X. Xie, L. Dai, Z. Wang, W. Wu, F. Zhao, X. Xie, S. Huang, M. Liu, S. Chen, Full-scale blending treatment of fresh MSWI leachate with municipal wastewater in a wastewater treatment plant, Waste Manage., 34 (2014) 2305–2311.
[34] D. Kulikowska, E. Klimiuk, The effect of landfill age on municipal leachate composition, Bioresour. Technol., 99 (2008) 5981–5985.
[35] R. Ayeche, Treatment by coagulation-flocculation of dairy wastewater with the residual lime of National Algerian Industrial Gases Company (NIGC-Annaba), Energy Procedia, 18 (2012) 147–156.
[36] H.J. Mansoorian, A.H. Mahvi, A.J. Jafari, Removal of lead and zinc from battery industry wastewater using electrocoagulation process: influence of direct and alternating current by using iron and stainless steel rod electrodes, Sep. Purif. Technol., 135 (2014) 165–175.
[37] J. Duan, J. Gregory, Coagulation by hydrolyzing metal salts, Adv. Colloid Interface, 100–102 (2003) 475–502.
[38] E. Bazrafshan, F. Kord Mostafapour, M. Alizadeh, M. Farzadkia, Dairy wastewater treatment by chemical coagulation and adsorption on modified dried activated sludge: a pilot-plant study, Desal. Wat. Treat., 57 (2016) 8183–8193.
[39] J.P. Kushwaha, V.C. Srivastava, I.D. Mall, Treatment of dairy wastewater by inorganic coagulants: parametric and disposal studies, Water Res., 44 (2010) 5867–5874.
[40] M. Vedrenne, R. Vasquez-Medrano, D. Prato-Garcia, B.A. Frontana-Uribe, J.G. Ibanez, Characterization and detoxification of a mature landfill leachate using a combined coagulation–flocculation/photo Fenton treatment, J. Hazard. Mater., 205 (2012) 208–215.
[41] E. Bazrafshan, M.R. Alipour, A.H. Mahvi, Textile wastewater treatment by application of combined chemical coagulation, electrocoagulation, and adsorption processes, Desal. Wat. Treat., 57 (2016) 9203–9215.
[42] E. Bazrafshan, F. Kord Mostafapour, A.H. Mahvi, Phenol removal from aqueous solutions using pistachio nut shell ash as a low cost adsorbent, Fresenius Environ. Bull., 21 (2012) 2962–2968.

[43] E. Bazrafshan, F. Kord Mostafapour, A.R. Hosseini, A. Rakhsh Khorshid, A.H. Mahvi, Decolorisation of reactive red (120) dye by using single-walled carbon nanotubes in aqueous solutions, J. Chem., 2013 (2013) 1–8.
[44] E. Bazrafshan, A.A. Zarei, H. Nadi, M.A. Zazouli, Adsorptive removal of methyl orange and reactive red 198 by *Moringa peregrina* ash, Indian J. Chem. Technol., 21 (2014) 105–113.
[45] P.M. Ramya, M. Jayasravanthi, B.J. Dulla, N.R. Venkata, Chemical oxygen demand reduction from coffee processing waste water – a comparative study on usage of biosorbents prepared from agricultural wastes, Global NEST J., 17 (2015) 291–300.
[46] M. Kilic, E. Apaydin-Varol, A.E. Putun, Adsorptive removal of phenol from aqueous solutions on activated carbon prepared from tobacco residues: equilibrium, kinetics and thermodynamics, J. Hazard. Mater., 189 (2011) 397–403.
[47] M.D. Ahmaruzzaman, Adsorption of phenolic compounds on low-cost adsorbents: a review, Adv. Colloid Interface Sci., 143 (2008) 48–67.
[48] E. Bazrafshan, A.A. Zarei, F.K. Mostafapour, Biosorption of cadmium from aqueous solutions by *Trichoderma* fungus: kinetic, thermodynamic, and equilibrium study, Desal. Wat. Treat., 57 (2016) 14598–14608.
[49] E. Bazrafshan, M. Ahmadabadi, A.H. Mahvi, Reactive Red-120 removal by activated carbon obtained from cumin herb wastes, Fresenius Environ. Bull., 22 (2013) 584–590.
[50] N. Gupta, S.S. Amritphale, N. Chandra, Removal of Zn (II) from aqueous solution by using hybrid precursor of silicon and carbon, Bioresour. Technol., 101 (2010) 3355–3362.
[51] A.A. Jalil, S. Triwahyono, S.H. Adam, N.D. Rahim, M.A. Aziz, N.H. Hairom, N.A. Razali, M.A. Abidin, M.K. Mohamadiah, Adsorption of methyl orange from aqueous solution onto calcined Lapindo volcanic mud, J. Hazard. Mater., 181 (2010) 755–762.
[52] E. Bazrafshan, F. Kord Mostafapour, S. Rahdar, A.H. Mahvi, Equilibrium and thermodynamics studies for decolorization of Reactive Black 5 (RB5) by adsorption onto MWCNTs, Desal. Wat. Treat., 54 (2015) 2241–2251.
[53] A.B. Zaki, M.Y. El-Sheikh, J. Evans, S.A. El-Safty, Kinetics and mechanism of the sorption of some aromatic amines onto amberlite IRA-904 anion-exchange resin, J. Colloid Interface Sci., 221 (2000) 58–63.
[54] E. Errais, J. Duplay, F. Darragi, I. M'Rabet, A. Aubert, F. Huber, G. Morvan, Efficient anionic dye adsorption on natural untreated clay: kinetic study and thermodynamic parameters, Desalination, 275 (2011) 74–81.