Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1029525

57 (2016) 9082–9092
April

Pilot-scale treatment of textile wastewater by combined biological-adsorption process

Seyed Ahmad Mirbagheri, Ali Charkhestani*

Civil and Environmental Engineering Faculty, Khaje Nasir University of Technology, Vali-e-asr Ave, 1996715433 Tehran, Iran, Tel. +98 9121374357; email: Mirbagheri@Kntu.ac.ir (S.A. Mirbagheri), Tel. +98 9106050469; email: Ali_Charkhestani@yahoo.com (A. Charkhestani)

Received 31 January 2014; Accepted 8 March 2015

ABSTRACT

Dye pigments are the main pollutants in textile industry wastewaters. Dye reduction or completely removal from the wastewater is the biggest challenge in this industry. This study was carried out by combined biological-adsorption system. Activated sludge with extended aeration as biological and slow filtration as adsorption process was used. In activated sludge system, different hydraulic retention times (HRT) were investigated (18, 24, 30, and 36 h). The results revealed that by increasing the HRT, the biological system could remove about 80% of chemical oxygen demand (COD) and 33.5% of dye pigments. Then the effluent of the biological system comes to the slow filtration pilot to remove the dye completely. In this stage, beside of granular activated carbon (GAC) that is very high-cost adsorbent, saw dust and inorganic soils, such as kaolin and talc were tested simultaneously. According to the results, the bed that contains GAC by 91%, kaolin 78%, saw dust 64.4%, and talc 55.5% removal showed the highest efficiency, respectively. Adsorption data were modeled using Langmuir and Freundlich isotherms. The analysis showed that Freundlich isotherm reasonably fit the experimental data for all the adsorbents. Finally, the combined biological-adsorption system could remove about 98.2, 95.6, 92.9, and 91.1% of COD by using GAC, kaolin, saw dust, and talc as an adsorbent, respectively. By considering the cost-benefit analysis and availability of the adsorbents, saw dust, and inorganic soils, such as kaolin can be the alternative choice instead of GAC to combine with activated sludge system in order to recycle the effluent of the textile industry wastewater and save huge amount of water.

Keywords: Textile wastewater; Activated sludge; Adsorption; GAC; Kaolin; Saw dust; Talc

1. Introduction

Textile industries require a considerable amount of water in their manufacturing processes. Most textile plants in Iran have been built in desert cities, such as Yazd, Kerman, and Kashan, where water shortage is a major problem [1]. Therefore, implementing an efficient treatment system for permitting the reuse of generated wastewater is considered as a national necessity and would be economically beneficial. According to conducted researches in the textile wastewater treatment methods, elimination of contaminations specially dye pigments is very difficult [2]. It has been proved that dyes are the most problematic compounds in the textile

*Corresponding author.

effluents because of their high water solubility and low exhaustion [3]. Also due to toxicity and carcinogenicity of some dye pigments, colored wastewater might have a harmful effect on ecosystem of water organisms [4].

Its strongest impact on the environment is related to primary water consumption (80–100 m^3/ton of finished textile) and wastewater discharge (115–175 kg of COD/ton of finished textile, a large range of organic chemicals, low biodegradability, color, and salinity) [5]. So removing these pigments from the wastewater thoroughly is one of the foremost concerns of the textile industry. To our knowledge, there is no single process capable of providing adequate treatment, mainly due to the complex nature of the effluents [6]. Most industrial wastewaters are treated with combination of treatment methods [7,8]. Many treatment processes have been applied for dye removal from wastewater, such as [9]: photocatalytic degradation [10,11], micellar-enhanced ultrafiltration [12], cation-exchange membranes [13], electrochemical degradation [14], adsorption-precipitation processes [15], integrated chemical–biological degradation [16], solar photo-Fenton and biological processes [17], and adsorption on activated carbon [18,19]. Some of these treatment methods may result in the production of toxic by-products or require high levels of energy, such as precipitation, flocculation, and membrane filtration [20].

Biological decolorization is a less-expensive and less environmentally intrusive alternative [20]. Also amongst the numerous techniques of dye removal, adsorption is one of the choices as it can be used to remove different types of dyes [9]. There are many publications on adsorption of dye with different types of adsorbents [21–23]. de Beltran and Gonzalez investigated necessary conditions to increase effects of ozone on wastewater color removal. They revealed that with relative pressure, proper temperature, and pH, elimination of color increased and the chemical oxygen demand (COD) reduction exceeded more than 60% [24]. Also Ergas et al. found out that the concern with ozone is high ozone doses, and large reactor volumes needed to achieve adequate color removal and the concern with electrochemical oxidation is the high chlorine residual and the possible generation of chlorinated organic by-products in the process [25]. Ganesh and Bordman treated more than 20 materials containing azo dyes by biological aeration system and indicated that in aeration system, initial elimination of color is done by adsorption [26].

The adsorption process is a successful technique for the removal of dyes. Erdem et al. investigated the removal of textile dyes by diatomite earth [27], and also Morais et al. did a research on reactive dyes removal from wastewater by adsorption of eucalyptus bark [28]. Lemlikchi et al. studied on possibility of using hydroxyapatite (HA) calcium phosphates as an economical reagent to purify textile dye, with constant HA/dye mass ratio of 20, the elimination yield was close to 97% for Dianix Red and 99% for Hydron Blue R [29]. Mittal and Venkobachar studied on adsorption of dye from textile wastewater by sulfonated coal. According to the results of basic and acidic color adsorption, the elimination yield was close to 99.8% for methylene blue (basic violet 9) and sandolan rhodine (acid red 1), and the adsorption follows Freundlich isotherm [30]. Errais et al. studied on textile dye removal by natural clay. The experimental results showed that the treatment by natural clay is more efficient than the conventional treatment by coagulation flocculation. For dyeing effluent containing direct, acid, and reactive dyes the COD dropped from 1,210 mg O_2/L to 471 mg O_2/L (a decrease of 61%) by the coagulation flocculation method with $Al_2(SO_4)_3$, while it reaches to 121 (a decrease of 90%) with natural clay which contains 60% smectites, 30% kaolinite and 10% illite, and 325.486 m^2/g specific surface area [31]. Also Lina and Wang declared that the color removal of the organobentonite was higher than that of the natural bentonite. The organobentonites were prepared by incorporating bentonite with a mixture of cationic and anionic surfactants with different ratio. The best color and COD removal at the dosing rate of 2 g/L, with the mass ratio of 4:1(anionic/cationic) was obtained as 70.8 and 68%, respectively [32]. Pala and Tokat found that addition of powdered activated carbon (PAC) to the mixed liquor of activated sludge treatment plants can be used to remove the color from wastewater. The results indicated that 100 mg/L PAC was sufficient to remove the maximum color measured (up to 50 m^{-1}) from the wastewater [33]. Eckenfelder declared that the COD and color removal efficiencies for only biological treatment for an industrial wastewater containing heavy metals, organic carbon, and color, were 28.6–67%, while the removal efficiencies with 50, 100, 250, and 500 mg/L PAC addition were 46–72, 69.2–78.4, 88.2–94, and 93–97.7%, respectively [34].

Adsorption processes are attractive due to their high efficiency, low-cost, availability, and easy design [35]. Although adsorption using activated carbon is attractive, owing to its high efficiency, it is a high-cost adsorbent. Recently, the natural inorganic and agricultural adsorbents have attained significant appeal [36]. By considering the benefit of biological treatment system, combination of this method with adsorption process might be effective.

In this study, efficiency of biological system has been investigated, and then four different adsorbents in tertiary treatment are compared. First, wastewater comes to extended aeration activated sludge system, where the pollution load is decreased. Then, the output of biological system goes to slow filtration pilot where adsorbent helps to remove dye completely and makes the effluent recyclable for dyeing and printing units.

The objective of this study is to investigate the dye removal of textile dyeing and printing unit wastewater using integrated biological-adsorption process. Most textile factory treatment plants use biological treatment alone, especially extended aeration activated sludge systems. However, activated sludge systems are not effective for complete dye removal from wastewater due to the textile dyes which are difficult to biodegrade [33]. So the adsorption process is added after the biological treatment as a tertiary treatment. In this research different hydraulic retention times (HRT) for biological system and four different adsorbents for adsorption process are investigated.

2. Materials and methods

In this research, the combination of two treatment methods is considered to design a more efficient treatment plant. These methods include biological treatment using extended aeration activated sludge joined with slow filtration with four different media in pilot scale. Reactive and disperse dyes are used in this experiment to simulate the behavior of dyes in real wastewater. The schematic layout of the experimental setup is shown in Fig. 1.

Design of bioreactor and characterization of filtration system are as follows:

2.1. Bench scale of activated sludge

(1) A 600 L tank equipped with control valve is used for feeding biological system in order to ensure constant flow rate.
(2) A plexiglass 45 L rectangular tank with dimension of 49 × 40 × 27 cm is used as the aeration tank.
(3) A plexiglass 80 L sedimentation rectangular tank is made in dimension 82 × 30 × 33 cm equipped with three volve.
(4) A lab scale surface aerator (72-895-30 type B) is used to supply and mix oxygen in aeration tank.
(5) Peristaltic pump for sludge recycling is used.

2.2. Preparation of activated sludge in the bench scale

Initially, for two weeks, synthetic wastewater are simulated and prepared using glucose as a carbon source, in order to reach at least the concentration of 3,000 mg/L suspended materials in the aeration tank (reactor). Composition of synthetic wastewater has been presented in Table 1.

Initial seeding of biological system is implemented by using activated sludge of Tehran refinery wastewater. Specification of this sludge is shown in Table 2. To reach the desired biomass concentration, real wastewater is replaced gradually by synthetic wastewater for 10 d. It means that the ratio of real wastewater to the synthetic wastewater is increased 10% per day, so after 10 d real wastewater is replaced with synthetic wastewater completely.

Specification of textile wastewater is presented in Table 3.

2.3. Filtration system

2.3.1. Filter frame

A 76 × 76 × 170 cm frame is used to locate different bed media. The frame is made of galvanized sheet with 2 mm thickness. The interior of frame is made of a 15 mm thick plexiglass, in order to facilitate observation of the bed. This frame was divided into two equal

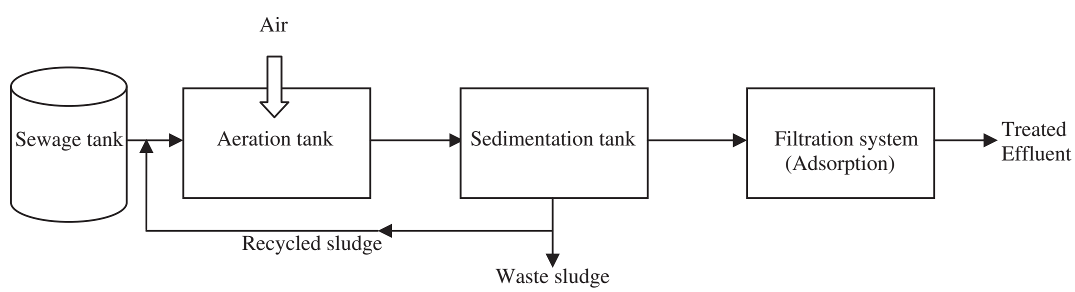

Fig. 1. The schematic layout of the experimental setup.

Table 1
Synthetic wastewater specification

Chemical material	Concentration (mg/L)
Magnesium sulfate $MgSO_4$, $7H_2O$	100
Ferric chloride, $FeCl_3$, $6H_2O$	0.5
Calcium chloride, $CaCl_2$	7.5
Manganese sulfate $MnSO_4$, H_2O	10.0
Potassium phosphate, monobasic, KH_2PO_4	275.0
Potassium phosphate, diabasic, $K_2H_2PO_4$	107.0

Table 2
Initial characterization of activated sludge for inoculation

Parameter	Ash (%)	Phosphorous (mg/L)	Total nitrogen (mg/L)	pH	MLSS (mg/L)	COD (mg/L)
	20	8.7	4.5	7.2	2,350	200

Table 3
Characterization of textile wastewater

Parameter	Range	Average
BOD (mg O_2/L)	220–260	240
COD (mg O_2/L)	615–675	645
Dye (mg/L)	–	65
Total nitrogen (mg/L)	104–196	150
Total phosphorous (mg P/L)	1.4–4.8	3.1
Suspended solid (mg/L)	–	160
VSS (mg/L)	–	148
pH	6–8.5	7.25
Conductivity (mohs/cm)	2,248–2,974	2,611
Total hardness (mg/L)	As$CaCO_3$	198
Cr (mg/L)	–	0.4
Zn (mg/L)	–	0.2
Fe (mg/L)	–	0.1
Ni (mg/L)	–	0.2
Cu (mg/L)	–	0.2
Pb (mg/L)	–	0.5

parts by a flat glass and sealed completely to compare two different media simultaneously.

2.3.2. Adsorbents

In this research, four different adsorbents (granular activated carbon, saw dust, kaolin, and talc) are used to compare their efficiencies in dyeing removal when they are placed after biological treatment. Granular activated carbon used is supplied by Jacobi Co., Ltd with density of 0.45 g/cm^3, 52% porosity, and 1,050 m^2/g specific surface area. Next, washed fine sawdust with average size of 3 mm, density of 0.198 g/cm^3, 1.71 m^2/g specific surface area, and 91% porosity is used. Sawdust is easily available in the countryside at zero or negligible price [37]. It contains various organic compounds (lignin, cellulose, and hemicellulose) with polyphenolic groups that might be useful for binding dyes through different mechanisms [38]. Two hundred mesh kaolin was provided by Iran China Clay Co, with the following characteristic: kaolin is one of the common low-cost natural clay adsorbents with ($Al_2O_7Si_2{\cdot}2H_2O$) molecular formula, 1,750˚C melting point, 258.16 molecular weight, 2.23 m^2/g specific surface area, and 2.6 g/cm^3 density. Mesh talc of 200–240 was provided by Chengdu XiYa Chemical Technology Co., Ltd with the following characteristics: ($Mg_3Si_4O_{10}(OH)_2$) molecular formula, 800˚C melting point, 379.27 molecular weight, 3 m^2/g specific surface area, and 2.7 gr/cm^3 density.

Five gravel layers in different size (18–36, 6–12, 2–4, 0.7–1.4, and 0.2–0.4 mm) are located at the bottom of the bed to prevent the media washout by wastewater, in addition to holding and supporting of media. The experiments are done using a two-layer metal frame containing five small holes with 2 mm diameter in different heights (5, 10, 20, 40, and 70 cm), so the relationship between the height of the bed and the rate of treatment is investigated. Actually five different adsorbent dose (10, 20, 40, 60, and 80 g/L) are contacted with the wastewater in each level, respectively. Table 4 shows the characterization of bench scale filtration system using different media in decolorization of wastewater.

Table 4
Characterization of different Filter systems

Filter parameter	Filter no 1	Filter no 2	Filter no 3	Filter no 4
Specific weight (g/cm^3)	0.450	0.198	2.6	2.7
Specific surface area (m^2/g)	1,050	1.71	2.23	3
Mesh	–	200	200	200
Gravel depth (cm)	50	50	50	50
Media depth (cm)	50	50	50	50
Flow rate (m^3/day)	0.38	0.38	0.38	0.38
Treatment rate (m^3/h)	0.12	0.12	0.12	0.12
Retention time on the bed (h)	2.5	2.5	2.5	2.5

Note: Filter no 1: Granular activated carbon, filter no 2: saw dust, filter no 3: kaolin, filter no 4: talc.

2.4. Sampling and analysis

To evaluate system operation and to monitor the pilot, wastewater parameters, such as COD, mixed liquor volatile suspended solids (MLVSS), sludge volume index (SVI), and pH are measured.

2.4.1. Measurement of COD

The COD is the measure of the oxygen equivalent of the organic material in water that can be oxidized chemically using dichromate in an acid solution. The sample is refluxed with potassium dichromate and sulfuric acid in the presence of mercuric sulfate (to neutralize the effect of chlorides) and silver sulfate (catalyst). The excess potassium dichromate is titrated against ferrous ammonium sulfate using ferroin as an indicator. The amount of potassium dichromate used is proportional to the oxidizable organic matter present in the sample. The COD is given by the following relation:

$$\mathrm{COD} = \frac{(b-a)\times(N)\,\text{of ferrous ammonium sulphate}\times 1{,}000\times 8}{\text{Volume (in mL) of sample}}\ \mathrm{mg/L} \tag{1}$$

where b is the volume (mL) of titrant using blank and a is the volume (mL) of titrant using the sample. To investigate COD removal efficiency of aeration and sedimentation tank, this test is carried out daily.

2.4.2. Measurement of pH

The pH of a solution measures the degree of acidity or alkalinity relative to the ionization of water sample. To investigate the changes, pH of the tanks is measured daily by 1,228 pH-meter H-5 model.

2.4.3. Measurement of MLVSS

The MLVSS represents the population size of bacteria within the activated sludge process. Volatile suspended solids are solids that burn in a muffle furnace at 550°C. Although, bacteria and other organic materials, for example, grease, oils, and particulate materials, burn in the muffle furnace at 550°C, it is assumed that all volatile solids are bacteria. Therefore, an increase in volatile content of the mixed liquor suspended solids (MLSS) represents an increase in the bacterial population, whereas a decrease in volatile content of the MLSS represents a decrease in the bacterial population. This parameter is used to determine the status of biological system and concentration of the micro-organisms in the aeration tank.

2.4.4. Measurement of SVI

The SVI is the volume in milliliters occupied by 1 g of a suspension after 30 min of settling. SVI typically is used to monitor settling characteristics of activated sludge and other biological suspensions. Although, SVI is not supported theoretically, experience has shown it to be useful in routine process control.

$$\mathrm{SVI} = \frac{\text{Settled sludge volume}\left(\frac{\mathrm{mL}}{\mathrm{L}}\right)\text{after 30 min}}{\text{Suspended solids}} \times \frac{1{,}000\,\mathrm{mg}}{\mathrm{g}} \tag{2}$$

2.4.5. Measurement of concentration of the dyes

The samples are analyzed by a UV spectrophotometer (Cl-45240-00) supplied by Motic, China with accuracy wave length of 2 nm from 400 to 700 nm and 3 nm from 700 to 900 nm for the measurement of dye removal. The maximum wavelength (λ_{max}) for the determination of residual dye concentration in solution was 595 nm.

2.4.6. Adsorption isotherm models

The equilibrium adsorption of effluent onto different adsorbent are analyzed using Langmuir and Freundlich isotherms. Langmuir and Freundlich isotherms are the earliest and simplest known relationships describing the adsorption equation.

2.4.6.1. Langmuir isotherm. Langmuir model is the simplest theoretical model for monolayer adsorption onto a surface with finite number of identical sites [39]. The general Langmuir equation is as follows:

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

When linearized, (Eq. (3)) becomes:

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_l} + \frac{1}{Q_m} C_e \tag{4}$$

where q_e is the amount of dye adsorbed on the adsorbent at equilibrium (mg/g), C_e is the liquid phase concentration of the adsorbate at equilibrium (mg/L), K_l is the Langmuir constant related to the adsorption energy, and Q_m is the maximum adsorption capacity (mg/g).

2.4.6.2. Freundlich isotherm. Freundlich expression is an empirical equation applicable to non-ideal sorption on heterogeneous surface as well as multilayer sorption [39]. The model is given as:

$$q_e = K_f C_e^{1/n} \tag{5}$$

Eq. (5) is linearized into logarithmic form for data fitting and parameter evaluation as follows:

$$\ln q_e = \ln K_f + 1/n \ln C_e \tag{6}$$

where K_f is the adsorption capacity at unit concentration and $1/n$ is the adsorption intensity.

3. Results and discussion

3.1. Adaptation period in biological pilot

During 13 d of monitoring including 3 d before and 10 d during the adaptation period, micro-organisms become compatible with new conditions. During the first few days of the adaptation period, an immediate feeding of real textile wastewater to the aeration tank and consequently an instant conversion of the carbon source from glucose to toxic and complex organic compounds, will distress the micro-organisms and drastically reduce their counts which results in the significant yield reduction of treatment.

Due to the presence of glucose in the first three days before the adaptation period, the efficiency of the system is approximately 94%, but it decreases immediately at the beginning of the ten-day adaptation phase to 71.7 and 54.2% in the first two days, respectively. However, since the third day of adaptation period, a yield increase is observed and reached the constant average of 67.8% at the end of this period. The yield curve shows this increase in Fig. 2. The reason of the yield reduction during the first two days of compatibility periods is the lack of the micro-organisms' adaptation to new conditions and resulting shock. In other words, the efficiency of the system is declined from 94% at the beginning of the compatibility period to the approximate value of 67.8% at the end of this period which seems reasonable according to the supply change and replacement of glucose with colored wastewater including complex organic materials. Table 5 shows the biological pilot operation in lab-scale during the adaptation period.

3.2. Activated sludge system

In the activated sludge system, after reaching to the steady state, the efficiency of dye, COD, and BOD removal under different HRT (18, 24, 30, and 36 h) are investigated (Tables 6 and 7). As demonstrated in the Table 7, the efficiency of BOD removal increases with the raising of the HRT. After 36 h, the BOD removal

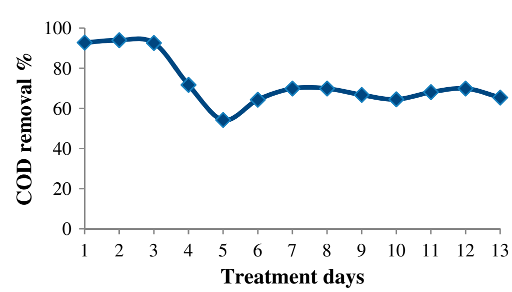

Fig. 2. COD removal efficiency during adaptation period.

Table 5
System operational result during adaptation

Parameter	Day 1	2	3	4	5	6	7	8	9	10	11	12	13
COD loading (kg COD/m^3/d)	0.733	0.748	0.789	0.733	0.740	0.762	0.752	0.789	0.768	0.727	0.821	0.843	0.853
COD inlet (mg/L)	580	576	592	580	555	572	564	592	576	620	616	632	640
COD outlet (mg/L)	42	34	44	164	254	204	170	178	192	220	196	190	222
COD removal %	92.8	94	92.6	71.7	54.2	64.3	69.9	69.9	66.7	64.5	68.1	69.9	65.4
MLSS (mg/L)	3,223	3,201	3,426	3,426	3,367	3,422	3,414	3,492	3,519	3,714	3,743	3,686	3,748
MLVSS (mg/L)	2,704	2,741	2,788	2,932	2,900	2,965	2,959	3,038	3,104	3,260	3,294	3,262	3,280
MLVSS %	83.9	85.6	85.9	85.6	86.1	86.6	86.7	87.0	88.2	87.8	88	88.5	87.6
F/M ratio [(kg COD/day)/kg MLVSS]	0.271	0.280	0.283	0.264	0.255	0.257	0.254	0.260	0.247	02.54	0.249	0.258	0.261
SVI (mg/g)	325	305	311	299	306	298	250	218	183	190	200	170	164

Table 6
The system's parameters during different HRT

Parameter	Hydraulic retention time (h) 18	24	30	36
Volumetric loading [kg COD/m^3 d]	0.857	0.640	0.257	0.441
F/M ratio [(kg COD/d)/kg MLVSS]	0.228	0.182	0.162	0.123
MLVSS (mg/L)	3,660	3,300	3,100	3,200
MLSS (mg/L)	3,900	3,600	3,500	3,600

Table 7
The average performance of the biological system during different HRT

Parameter	Initial	Hydraulic retention time (h) 18	24	30	36
COD (mg/L)	645	250	200	148	128
COD removal %		61.2	69.0	77.1	80.2
Dye (mg/L)	65	53.8	50.25	46.0	43.2
Dye removal %		17.2	22.7	29.2	33.5
BOD (mg/L)	240	32	24	19	5
BOD removal %		86.7	90.0	92.1	97.9
SVI (mg/g)		159	123	99	90

efficiency became 97.9% and BOD of wastewater reached 5 mg/L, thus the system could eliminate BOD completely. COD removal follows the same pattern with the raising of the HRT, but it shows a lower efficiency in comparing with BOD, due to the presence of many complex organic compounds in the wastewater which are not simply degraded. Under the best condition, 80% of COD is removed. The percentage of dye removal in aeration and sedimentation units with different HRT is shown in Fig. 3.

3.3. Adsorption in slow filtration system

The results of dye removal by different adsorbents are shown in Fig. 4. The average of dye concentration vs. depth of bed is calculated during 21 d. According to the obtained results in Fig. 4, the best efficiency of dye removal is related to granular activated carbon bed (91.1%) which is followed by kaolin (77.8%), saw dust (64.4%) and talc (55.5%), respectively. The difference in efficiency of inorganic soils (kaolin and talc) depends on chemical structure of adsorbent materials and adsorption mechanism.

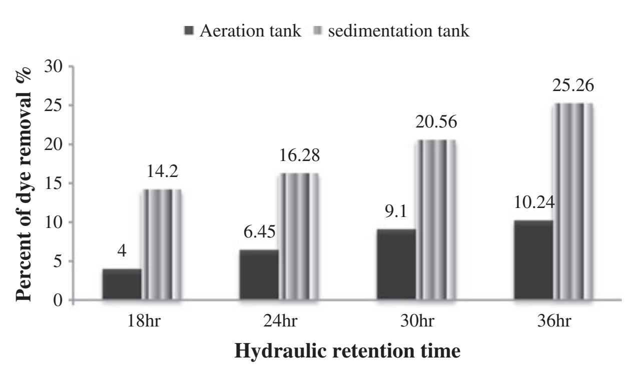

Fig. 3. The dye removal percentage in different part of biological system.

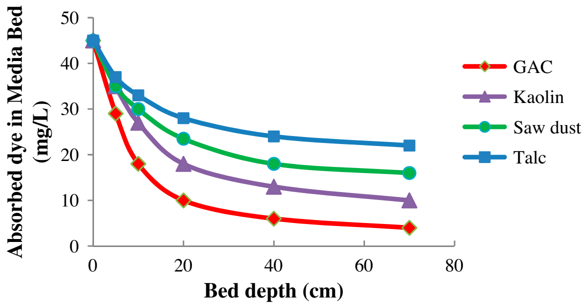

Fig. 4. Adsorbed dye vs. different bed depths.

3.4. Economic performance

Table 8 shows the cost-benefit analysis for removal of one gram dye from the textile wastewater by different adsorbents. The results indicate that the cost ratio for removal of one gram dye using activated carbon in comparison with saw dust is 30 to 1. Considering that the saw dust of fine wood particles are commercially available almost everywhere, treating textile wastewater with the filter media mostly packed with fine wood particles as tertiary treatment is recommended. In addition, kaolin is one of the common low-cost natural clay adsorbents with high removal efficiency, so it is another choice as an adsorbent in filtration system instead of granular activated carbon (GAC).

Table 8
Economic analysis of the adsorbents

Adsorbent	Price of removing one gram of dye (Rial)
GAC	4,500
Kaolin	840
Talc	250
Saw dust	140

3.5. Adsorption study

Although, it is well known that the Langmuir equation is intended for the homogenous surface, Freundlich equation is suitable for a highly heterogeneous surface. According to the Eqs. (4) and (6), the experimental data are fitted into the both Langmuir and Freundlich isotherms. The linear regression equations and determination coefficient (R^2) generated are shown in Figs. 5–8.

As shown in these figures, GAC and kaolin follows the Freundlich and Langmuir isotherms, but saw dust and talc just follow Freundlich isotherm. For all adsorbents, the values of R^2 in the Freundlich isotherm is higher than Langmuir isotherm, it means that Freundlich model gives a better fit to the adsorption. Freundlich equation gives an adequate description of adsorption data over a restricted concentration.

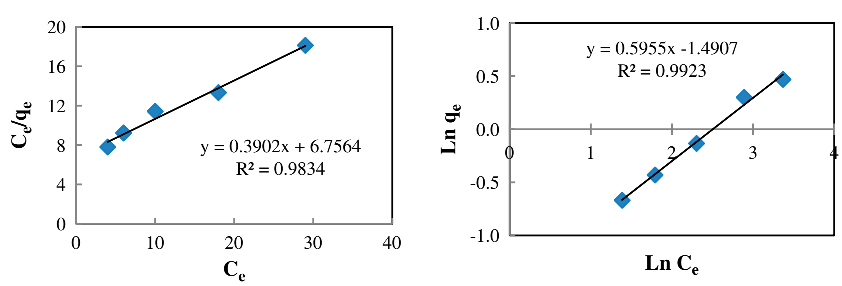

Fig. 5. Langmiur and Freundlich adsorption isotherms for GAC.

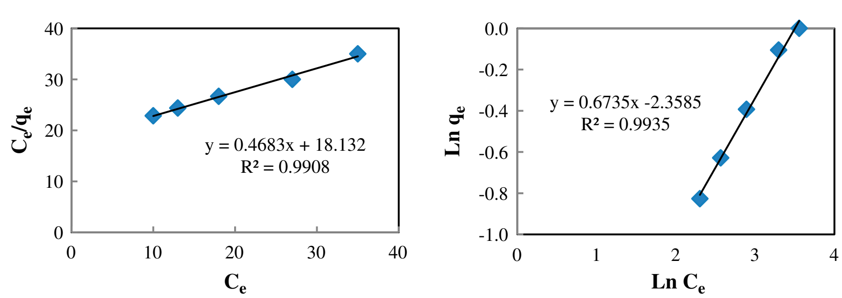

Fig. 6. Langmiur and Freundlich adsorption isotherms for kaolin.

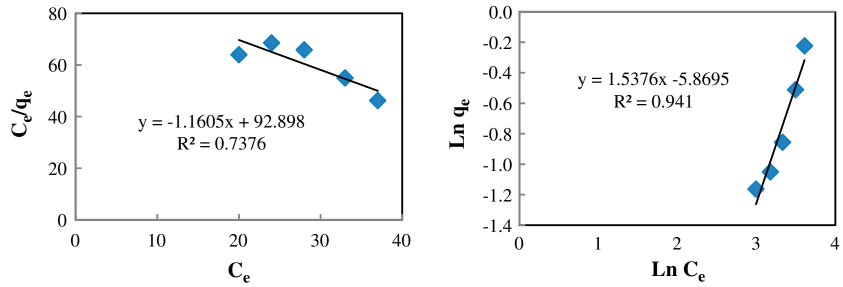

Fig. 7. Langmiur and Freundlich adsorption isotherms for talc.

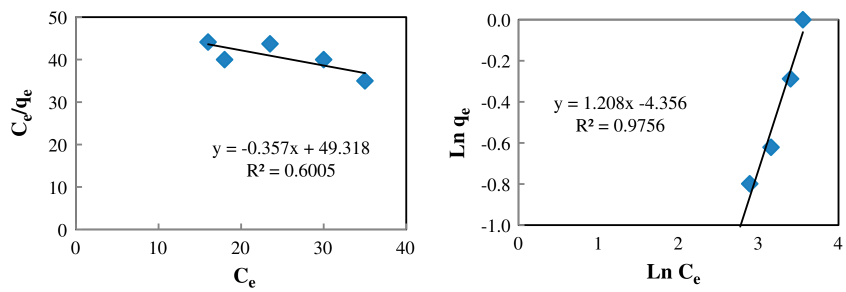

Fig. 8. Langmiur and Freundlich adsorption isotherms for saw dust.

Because of better fitting of the adsorbents in the Freundlich isotherm, the isotherm constants are shown in Table 9. The values of $1/n$ less than the unity for both GAC and Kaolin which is an indication that significant adsorption takes place at low concentration but the increase in the amount adsorbed with concentration becomes less significant at higher concentration. The values of K_f confirm that the adsorption capacity of GAC is higher than that in case of other adsorbents as the higher the K_f value, the greater the adsorption intensity.

It must be mentioned that because of decreasing the operational costs for the textile industries, all the adsorbents in this research were used in natural condition without any modification, activation processes, changing in pH, or other activities to improve their removal efficiency.

Table 9
Freundlich isotherm constants for dye adsorption onto the adsorbents

Adsorbent	Freundlich isotherms constant		
	n	K_f	R^2
GAC	1.681	0.225	0.992
Kaolin	1.486	0.094	0.994
Saw dust	0.828	0.013	0.976
Talc	0.6504	0.003	0.941

4. Conclusions

To sum up, the treatment of textile wastewater with the objective of dye removal to recycle the effluents in the textile industry was studied and presented in this paper. The activated sludge system with extended aeration method was used for the removal of BOD, COD, and other pollutants as a primary treatment. This system evaluated in different HRT (18, 24, 30 and 36 h), and finally could remove about 80% of COD and 34% of dye (at 36 h). Then slow filtration pilot was used as a tertiary treatment for the complete dye removal of the primary treatment effluent. Also in this stage, to find an alternative choice instead of GAC, other adsorbent such as kaolin, talc, and saw dust were compared as a filter media in the same conditions without any activation processes. As we expected, GAC with 91.1% in dye removal showed the best efficiency, but the high-cost restricted its use. On other hand, kaolin, saw dust, and talc showed 77.8, 64.4, and 55.5% removal efficiency, respectively. Finally, by testing the effluent of combined biological-adsorption system, this system removed 98.2, 95.6, 92.9, and 91.1% of COD using GAC, kaolin, saw dust, and talc, respectively.

The analysis of experimental isotherms showed that the adsorbents were best fitted to the Freundlich isotherm. In the case of saw dust and talc, they just fitted to the Freundlich isotherm but GAC and kaolin reasonably followed the Langmuir isotherm, too.

Economic performance of the adsorbents to remove one gram of dye showed the big gap between GAC and other adsorbents (more than 30 times). So by considering the cost-benefit analysis and availability of the adsorbents, saw dust, and inorganic soils, such as kaolin can be the best alternative instead of GAC to combine with activated sludge system in order to recycle the effluent of textile industry.

References

[1] K. Kamran, Optimization Studies of Textile Wastewater Treatment Methods, Second International Symposium on Environmental Engineering, Tehran, Iran, 2003, pp. 75–76 (in Persian).
[2] T.T. Teng, L.W. Low, Advances in Water Treatment and Pollution Prevention, Springer, Netherlands, 2012, pp. 65–93.
[3] F. He, W. Hu, Y. Li, Biodegradation mechanisms and kinetics of azo dye 4BS by a microbial consortium, Chemosphere 57 (2004) 293–301.
[4] C. O'Neill, F. Hawkes, D.L. Hawkes, N.D. Lourenço, H.M. Pinheiro, W. Delée, Colour in textile effluents-sources, measurement, discharge consents and simulation: A review, J. Chem. Technol. Biotech. 74 (1999) 1009–1018.
[5] I.I. Savin, R. Butnaru, Wastewater characteristics in textile finishing mills, Environ. Eng. Manage. J. 7 (2008) 859–864.
[6] A. Marco, S. Esplugas, G. Saum, How and why combine chemical and biological processes for wastewater treatment, Water Sci. Technol. 35 (1997) 321–327.
[7] L.D. Benefeild, C.W. Randall, Biological Process Design for Wastewater Treatment, Prentice-Hall, Ink, 1980, p. 526.
[8] S.H. Lin, C.F. Peng, Continuous treatment of textile wastewater by combined coagulation, electrochemical oxidation and activated sludge, Water Res. 30 (1996) 587–592.
[9] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of methylene blue on low-cost adsorbents: A review, J. Hazard. Mater. 177 (2010) 70–80.
[10] M.R. Sohrabi, M. Ghavami, Photocatalytic degradation of Direct Red 23 dye using UV/TiO_2: Effect of operational parameters, J. Hazard. Mater. 153 (2008) 1235–1239.
[11] M. Sleiman, D.L. Vildozo, C. Ferronato, J.M. Chovelon, Photocatalytic degradation of azo dye metanil yellow: Optimization and kinetic modeling using a chemometric approach, Appl. Catal., B. 77 (2007) 1–11.
[12] N. Zaghbani, A. Hafiane, M. Dhahbi, Removal of Safranin T from wastewater using micellar enhanced ultrafiltration, Desalination 222 (2008) 348–356.
[13] J.S. Wu, C.H. Liu, K.H. Chu, S.Y. Suen, Removal of cationic dye methyl violet 2B from water by cation exchange membranes, J. Membr. Sci., 309 (2008) 239–245.
[14] L. Fan, Y. Zhou, W. Yang, G. Chen, F. Yang, Electrochemical degradation of aqueous solution of Amaranth azo dye on ACF under potentiostatic model, Dyes Pigm. 76 (2008) 440–446.
[15] M.X. Zhu, L. Lee, H.H. Wang, Z. Wang, Removal of an anionic dye by adsorption/precipitation processes using alkaline white mud, J. Hazard. Mater. 149 (2007) 735–741.
[16] G. Sudarjanto, B. Keller-Lehmann, J. Keller, Optimization of integrated chemical–biological degradation of a reactive azo dye using response surface methodology, J. Hazard. Mater. 138 (2006) 160–168.
[17] J. García-Montaño, L. Pérez-Estrada, I. Oller, M.I. Maldonado, F. Torrades, J. Peral, Pilot plant scale reactive dyes degradation by solar photo-Fenton and biological processes, J. Photochem. Photobiol., A. 195 (2008) 205–214.
[18] B.H. Hameed, F.B.M. Daud, Adsorption studies of basic dye on activated carbon derived from agricultural waste: *Hevea brasiliensis* seed coat, Chem. Eng. J. 139 (2008) 48–55.
[19] F.C. Wu, R.L. Tseng, High adsorption capacity NaOH-activated carbon for dye removal from aqueous solution, J. Hazard. Mater. 152 (2008) 1256–1267.
[20] R. Żyłła, J. Sójka-Ledakowicz, E. Stelmach, S. Ledakowicz, Coupling of membrane filtration with biological methods for textile wastewater treatment, Desalination 198 (2006) 316–325.
[21] P.S. Joaquim, Adsorption of acid orange 7 dye in aqueous solutions by spent brewery grains, Sep. Purif. Technol. 40 (2004) 309–315.
[22] S. Mommura, Influence of resin-adsorption as pre-treatment on performance in anaerobic followed by aerobic treatments of synthetic textile wastewater, J. Biosci. Bioeng. 95 (2003) 428.
[23] S.A. Figueiredo, R.A. Boaventura, J.M. Loureiro, Color removal with natural adsorbents: Modeling, simulation and experimental, Sep. Purif. Technol. 20 (2000) 129–141.
[24] H. de Beltran, J.R. Gonzalez, Acid dye ozonation effect of variables and reduction products, Afinidad 47 (1990) 116–120.
[25] S.J. Ergas, B.M. Therriault, D.A. Reckhow, Evaluation of water reuse technologies for the textile industry, J. Environ. Eng. 132 (2006) 315–323.
[26] R. Ganesh, G. Boardman, Fate of azo dyes in sludges, Water Res. 28 (1994) 1367–1376.
[27] E. Erdem, G. Çölgeçen, R. Donat, The removal of textile dyes by diatomite earth, J. Colloid Interface Sci. 282 (2005) 314–319.
[28] L.C. Morais, O.M. Freitas, E.p Gonçalves, L.T. Vasconcelos, C.G. González Beça, Reactive dyes removal from wastewaters by adsorption on eucalyptus bark: Variables that define the process, Water Res. 33 (1999) 979–988.
[29] W. Lemlikchi, P. Sharrock, M.O. Mecherri, M. Fiallo, A. Nzihou, Reaction of calcium phosphate with textile dyes for purification of wastewaters, Desalin. Water Treat. 52 (2014) 1669–1673.
[30] A. Mittal, C. Venkobachar, Sorption and desorption of dyes by sulfonated coal, J. Environ. Eng. 119(2) (1993) 366–368.

[31] E. Errais, J. Duplay, F. Darragi, Textile dye removal by natural clay—Case study of Fouchana Tunisian clay, Environ. Technol. 31 (2010) 373–380.
[32] J.X. Lina, L. Wang, Treatment of textile wastewater using organically modified bentonite, Desalin. Water Treat. 25 (2011) 25–30.
[33] A. Pala, E. Tokat, Activated carbon addition to an activated sludge model reactor for color removal from a cotton textile processing wastewater, J. Environ. Eng. 129 (2003) 1064–1068.
[34] W.W. Eckenfelder, Industrial Water Pollution Control, second ed., McGraw-Hill, Singapore, 1989.
[35] A.R. Tehrani-Bagha, H. Nikkar, N.M. Mahmoodi, M. Markazi, F.M. Menger, The sorption of cationic dyes onto kaolin: Kinetic, isotherm and thermodynamic studies, Desalination 266 (2011) 274–280.
[36] G. Crini, Non-conventional low-cost adsorbents for dye removal: A review, Bioresour. Technol. 97 (2006) 1061–1085.
[37] V.K. Garg, M. Amita, R. Kumar, R. Gupta, Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: A timber industry waste, Dyes Pigm. 63 (2004) 243–250.
[38] A. Shukla, Y.H. Zhang, P. Dubey, J.L. Margrave, S.S. Shukla, The role of sawdust in the removal of unwanted materials from water, J. Hazard. Mater. 95 (2002) 137–152.
[39] M.A. Abdullah, L. Chiang, M. Nadeem, Comparative evaluation of adsorption kinetics and isotherms of a natural product removal by Amberlite polymeric adsorbents, Chem Eng. J. 146 (2009) 370–376.