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Treatability of organized industrial district (OID) effluent for reuse in agriculture

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ABSTRACT

In this study, a combination of chemical precipitation, neutralization and ion exchange processes for an Organized Industrial District (OID) wastewater reclamation for reuse in agriculture was investigated. The parameters analyzed after treatment stages are agricultural irrigation standards. Optimum removal efficiencies for SS, COD, and fecal coliform bacteria were obtained as 96%, 31%, and 87%, respectively, when the pH value was adjusted to 11 in the chemical precipitation process. The average removal efficiency obtained for conductivity parameter was 90%, and the removal efficiencies for SO_4^{2-} and Cl– were 71% and 96%, respectively, when the resin with 20 mL H-type/ 20 mL OH-type ratio was used in the ion exchange process. As a result of the study, the quality of the water treated by using chemical precipitation and ion exchange processes was enough to be reused in agriculture.

Keywords: Chemical precipitation; Ion exchange; Organized industrial district; Agricultural irrigation; Reuse

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1. Introduction

The shortage of water resources of good quality has become an important issue in the arid and semi-arid regions. As taken of the fact that this long process has been completed, several countries today regularly face imbalances of water demand and water supply, especially in the summer period, due to simultaneous occurrence of low precipitation, high evaporation and increased demands for irrigation and tourism [1,2]. Not surprisingly, the decrease in resources in natural waters brought about by drought and population growth is inciting authorities to establish and to encourage the reuse of wastewater [3]. For example, in many parts of the world, such as United States, Australia, South Africa, Japan, Italy, Spain, and Tunisia, treated wastewater has been successfully used for irrigation and many researchers have recognized its benefits [4,5]. In particular in Mediterranean countries, the reuse of wastewater is undergoing fast expansion in areas with water scarcity and its application in agriculture is becoming an important addition to water supplies [6]. Wastewater is used as a common term to indicate water that has been used in domestic activities or in industrial processes. This implies that wastewater contains polluting elements, such as organic material, chemical substances, and often pathogens. Increasing urbanization and eco-

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nomical development lead to a higher water use in urban areas and a further increase of wastewater flows [7].

Application of treated wastewater for irrigation of plants and crops is gradually becoming a common practice worldwide [8–10]. It is beneficial for a number of reasons: (a) water shortage can be resolved; (b) large amounts of wastewater can be disposed of during the entire year; (c) high-quality resources could be used for potable uses; (d) economic benefits, attributed primarily to the nutrient content of the wastewater are possible [11].

Wastewater reclamation and reuse is of great interest and a viable option for many industrial sectors and countries which suffer from water scarcity problems [12,13]. It is expected that the promotion of an integrated approach to water resources management, as it is spelled out in the Water Framework Directive (WFD) (91/271/EEC and 2000/60/EC) [14], will favour municipal wastewater reclamation and reuse on a larger scale, both for augmenting water supply and decreasing the impact of human activities on the environment. Reuse activities are consolidated in four categories: 1) agricultural irrigation; 2) aquifer recharge, urban, recreational and environmental uses; 3) process water for industry including cooling and 4) combinations of the above (multipurpose schemes) [15]. Thus, wastewater reuse may strengthen water savings generating supplementary water sources, which are especially important in areas with limited rainfalls [16]. Over 3300 water reclamation facilities were identified, mostly in Japan and the USA, but also in Australia and the EU, with now an abundance of over 450 and 230 projects, respectively [17].

Although the amount of reusable domestic and industrial wastewater is much lower than the wastewater generated, many countries show an increasing interest in wastewater reclamation and reuse [18,19]. Hochstrat et al. [20] estimated that in the time span between 2000 (when the WFD was issued) and 2025, the direct utilization of treated municipal wastewater in Europe could more than double, passing from the current 750 Mm^3/y to 1540–4000 Mm^3/y. The annual total water potential in Turkey is 187 billion m^3, and 30–35 billion m^3 of this potential is directly used for irrigational purposes. According to the General Agricultural Census results of 2001, only 13.24% of the 37472 agricultural units in Turkey have sufficient irrigational opportunities. Although Turkey is known to have a significant water potential, treatment and reuse matters of wastewaters should be considered in order to avoid local water shortages and crises, because the water potential is not homogenous in terms of geographical location and time [21].

Various advanced wastewater treatment technologies have been proposed in the literature for the production of organized industrial district effluents with a quality complying with the specific applications of wastewater reclamation and reuse [22,23].

Hydroxide (OH^-) precipitation is a common chemical treatment method, having simple technology and low operational costs. Some basic chemicals used for hydroxide precipitation are NaOH, $Ca(OH)_2$ and $Mg(OH)_2$. Hydroxide precipitation with $Ca(OH)_2$ is a generally preferred method for treatment of industrial wastewater. Low operating cost, high treatment efficiency and application convenience are some of its advantages However, high amount of sludge formation is the main disadvantage of this process. [24,25].

Ion exchanger systems currently have widespread use for obtaining high quality water [26]. Some problems are encountered during their use (including. loading, backwashing and regeneration). Fouling is considered one of the important problems of ion exchange resins [27,28].

Variations depend on local situations and greatly vary due to the present wastewater infrastructure and regulations [29]. Each reuse option requires different water qualities which can be reached by using different levels of treatment (Fig. 1).

With agricultural reuse of wastewaters, the public health protection measures should be considered and recommended in the main strategic areas, and selected to suit local circumstances [31]. For reuse in agriculture, both the distinction between unrestricted and restricted irrigation and the kind of irrigation are important. When the reclaimed water is hygienically safe, it can be applied for unrestricted irrigation. Public health aspects are also predominant when irrigation is done with sprinklers. Re-

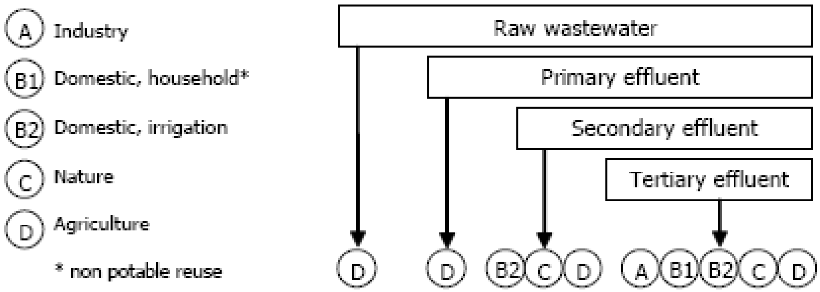

Fig. 1. Reuse aims with their corresponding levels of treatment [29,30].

gardless of the type and kind of irrigation the prevention of clogging and corrosion can be mentioned as functional aspects. When irrigating food crops, acceptance issues need attention [29].

In the context of this work, research was carried out to increase the quality of the wastewaters from an organized industrial district (OID) in Turkey to use for agricultural irrigation purposes. Chemical precipitation and ion exchange methods were applied.

2. Materials and methods

The wastewater collected at the common channel of the OID with a flow rate of 48,000 m^3/d is treated at the WWTP including chemical treatment and extended aerated-activated sludge units. Composite 2 h wastewater samples were taken at 3 different time periods from the effluent of the WWTP. The WWTP meets the discharge criteria enforced by Turkish Water Pollution Control Legislation (WPCL), however the treated wastewaters are discharged without any consideration for reusability. Experimental studies included chemical precipitation, neutralization, and ion exchange (Fig. 2).

2.1. Chemical precipitation and neutralization

Chemical precipitation and neutralization processes were conducted with jar test apparatus. The pH values of the wastewater samples of 1 L bottles were increased up to the levels between 10–12 by adding $Ca(OH)_2$. Rapid mix of 100 rpm was applied for 2 min and slow mix of 20 rpm was applied for 20 min after $Ca(OH)_2$ addition for the jar test procedure [32]. The waiting period to allow the precipitation of the flocks formed after the mixing was 90 min. After the waiting settling period the upper clear phase of the samples were taken and neutralized with 1 N H_2SO_4 to adjust the pH to 7.5±0.1.

2.2. Ion exchange resins

The experimental studies were conducted with different types of cation and anion exchange resins. 2 columns of 2 cm diameter and 45 cm height were used. The first column was filled with strong cationic resin and the second column was filled with strong anionic resin. The effluent from the chemical precipitation process was fed to the ion exchange resins by using a peristaltic pump (Heidolph Pumpdrive–5006). Technical specifications of the resins used in this study are given in Table 1.

The wastewater precipitated by adding $Ca(OH)_2$ was transferred with 4.2 m/h velocity through firstly cation exchange resin and then anion exchange resin. The cation exchanger was transformed from Na^+ form into H^+ form by using 8% HCl and the anion exchanger was transformed from Cl^- form into OH^- form by using 5% NaOH. pH and conductivity values were measured at the outlet of anion exchange resin to be able to compare the water quality obtained after different operating conditions for the resins.

2.3. Analysis methods

COD, BOD5, SS, Cl-, SO42–, and faecal coliform measurements of the water samples from different treatment stages were carried out according to the Standard Methods [33]. Heavy metals and toxic elements were measured with UNICAM 929 atomic absorption spectrophotometer.

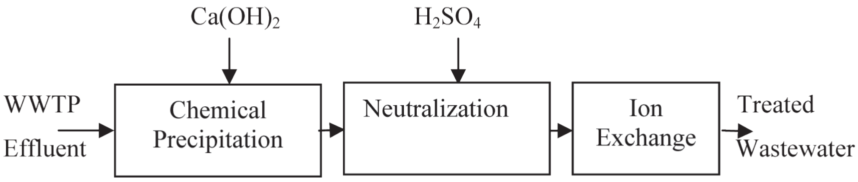

Fig. 2. Flowchart for experimental studies.

Table 1
Technical specifications of the ion exchange resins

Properties	Strongly acidic cation exchanger I	Strongly basic anion exchanger I	Strongly acidic cation exchanger II	Strongly basic anion exchanger II
Form	Na^+	Cl^-	Na^+	Cl^-
Functional group	Sulphonic acid	Quarternary amine Type 1	Sulphonic acid	Quarternary amine Type 1
Structure	Gel	Gel	Gel	Gel
Bead size (mm)	0.58	0.60	0.43	0.40

2.4. Characteristics of wastewater treatment plant effluent

The mean values for the wastewaters that were sampled in 3 different times from the effluent of the WWTP are given in Table 2.

Turkish WPCL defines 5 categories for the use of the waters for agricultural irrigation purposes (in Table 3), maximum heavy metal and toxic elements concentrations are given in Table 4 [34].

Table 2
Mean values of wastewater samples

Parameter (mg/L unless other unit is indicated)	Mean ± SD*
pH	7.4 ± 0.3
Temperature, °C	22 ± 4
COD	131 ± 18
SS	75 ±13
Sulphate	244 ± 45
Chloride	1282 ± 190
Conductivity, µS/cm	3590 ± 312
SAR	14.8 ± 1.4
BOD_5	20 ± 4
NO_3^-	27 ± 6
Fecal coliforms, MPN per 100 mL	440 ± 52
Metal content	
Fe	3.5 ± 0.3
Cu	0.11 ± 0.05
Cd	0.004
F	0.663 ± 0.04
Total Cr	0.075 ± 0.01
Zn	0.286 ± 0.03
Pb	0.162 ± 0.02

*SD: standard deviation.

As can be seen in Table 3 and Table 4, the wastewater samples meet the 1st class agricultural irrigation water standards in terms of BOD_5, metals, and pH. However SS, sulphate, chloride, conductivity, and faecal coliform values of the wastewater are above the regulated standards.

3. Results and discussion

3.1. Chemical precipitation process

Hydroxide precipitation was applied for chemical precipitation, and optimum pH was determined as an important operational parameter. Chemical precipitation at high pH (pH > 9.5) application was adopted in order to improve the wastewater quality and protect the capacity of ion exchange resins from the pollutant parameters such as COD, SS, and Fe [34–36]. The pH of the raw wastewater should increase up to the levels of 11–11.5 to achieve $Ca(CO)_3$ and $Mg(OH)_2$ precipitation together [37].

To determine the optimum pH levels for hydroxide precipitation in this study, the pH of the raw wastewater

Table 4
Maximum heavy metal and toxic element concentrations allowed for irrigational waters

Parameter (mg/L unless other unit is indicated)	Limit values for irrigation in all grounds
Fe	5
Cu	0.2
Cd	0.01
F	1
Total Cr	0.1
Zn	2
Pb	5

Table 3
Agricultural irrigation quality parameters

Parameter (mg/l unless other unit is indicated)	Agricultural irrigation class				
	I	II	III	IV	V
pH	6.5–8.5	6.5–8.5	6.5–8.5	6.5–9	<6 or >9
Temperature, °C	30	30	35	40	>40
SS	20	30	45	60	>100
BOD_5	0–25	25–50	50–100	100–200	>200
Sulphate	0–192	192–336	336–575	575–960	>960
Chloride	0–142	142–249	249–426	426–710	>710
NH_4^+ or NO_3^-	0–5	5–10	10–30	30–50	>50
Conductivity, µS/cm	0–250	250–750	750–2000	2000–3000	>3000
Fecal coliforms, MPN per 100 mL	0–2	2–20	20–100	100–1000	>1000

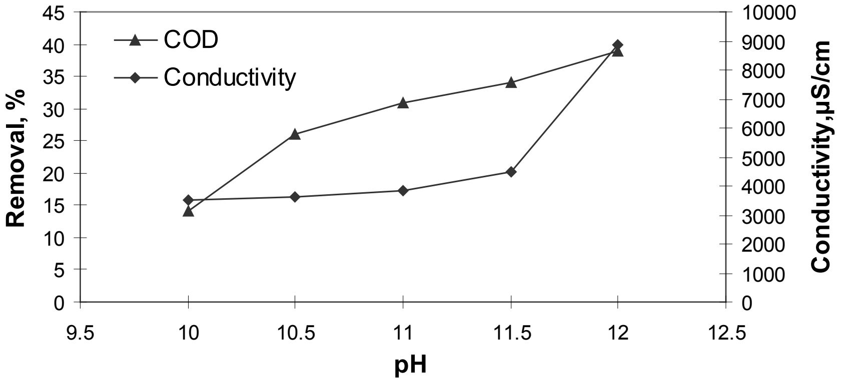

Fig. 3. COD removal efficiency obtained after increasing the pH of the wastewater by using $Ca(OH)_2$ and variations in the conductivity

samples were increased up to 10, 10.5, 11, 11.5, and 12, respectively, by using Ca(OH)2. The COD removal efficiency achieved and the mean of the conductivity values are given in Fig. 3.

As can be seen from Fig. 3, the COD removal efficiency increased from 14% to 39% as the pH values increased. The $Ca(OH)_2$ added increased the conductivity of the wastewater from 3500 µS/cm up to 8873 µS/cm at pH 12. After chemical precipitation, the optimum pH level was found to be 11 regarding the COD removal efficiency and the conductivity values of the wastewater that fed the resin columns. When the pH level was 11, the faecal coliform value decreased from 440 (MPN per 100 mL) down to 57 (MPN per 100 mL), which amounts to a removal efficiency of 87%.

3.2. Ion exchange process

Ion exchange is the best solution to decrease the conductivity and remove the inorganic ions [38]. After the chemical precipitation, the neutralized wastewaters were passed through the resin columns to remove the conductivity and inorganic ions, and achieve the irrigational water standards. Chemically precipitated wastewater by using $Ca(OH)_2$ was passed through the resin columns where the ratio of cation exchange/anion exchange was 20 mL/20 mL. The variations in the conductivity and pH are shown in Fig. 4 and Fig. 5, respectively.

In Fig. 4, the horizontal dotted line shows the legal standard level for conductivity for agricultural irrigation waters, which is 250 µS/cm. The horizontal dotted lines in Fig. 5 show the feasible pH interval for agricultural irrigation water, which is 6.5-8.5.

As can be seen from Fig. 5, more wastewaters could pass through the columns by using Resin I than that passed through Resin II, at 250 µs/cm standard. Similarly, Fig. 5 shows that Resin I was more successful than Resin II regarding the amount of the wastewater that could be passed at the standard pH interval of 6.5–8.5.

The changes in the quality of the wastewaters at each

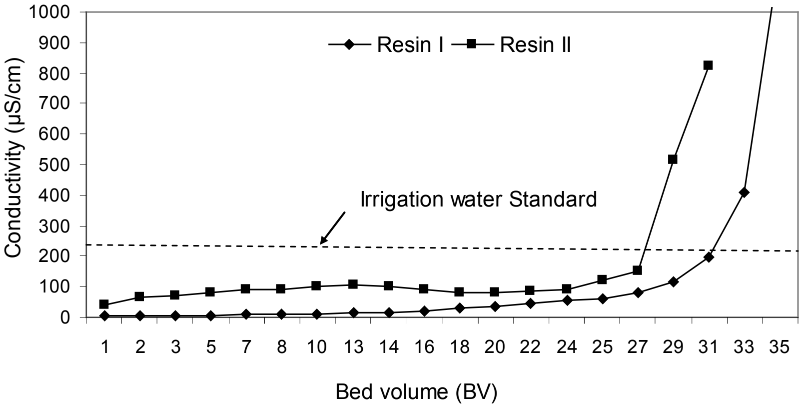

Fig. 4. The conductivity values for the wastewaters chemically precipitated by using $Ca(OH)_2$ and passed through Resin I and Resin II.

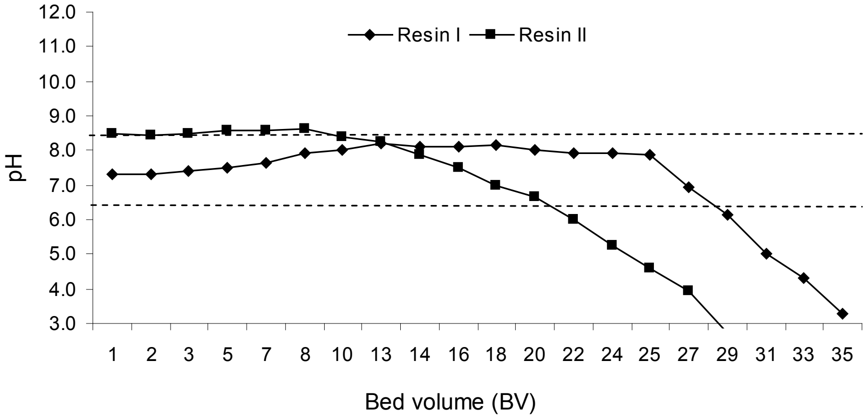

Fig. 5. The pH values of the wastewaters chemically precipitated by using $Ca(OH)_2$ and passed through Resin I and Resin II.

Table 5
Changes in the wastewater quality in each treatment step

Parameter (mg/l unless other unit is indicated)	Raw wastewater	Chemical precipitation	Ion exchange (Resin I)
pH	7.4±0.3	7.5±0.1	6.9±0.1
SS	75±13	3±1	0
BOD_5	20±4	13±2	4±1
NO_3^-	27±6	26±6	2.4±0.4
Sulphate	244±45	549±190	71±12
Chloride	1281±190	1168±179	53±7
Conductivity, µS/cm	3803±273	3590±211	191±36
Fecal coliforms, MPN per 100 mL	440±52	57±8	55±7

treatment stage considering the samples where the optimum pollutant removal efficiencies obtained after chemical precipitation and ion exchange are given in Table 5.

The parameters in Table 5 were composed considering the parameters that have lower values than the values of the 1st class water quality. The mean values of wastewater samples and standard deviation values were used to evaluate the results.

As can be seen from Table 5, the H_2SO_4 used for neutralization in chemical precipitation process causes the increase in sulphate ion concentration. The faecal coliform removal efficiencies obtained after the chemical precipitation process confirmed the results of similar studies from the literature [39–41]. Additionally, after the ion exchange process, all the parameters except for faecal coliform parameter met the standards for the 1st class irrigational water.

4. Conclusion

The reusability of the wastewaters that originated from an organized industrial district in Bursa, Turkey was investigated in this study. The wastewater samples were taken from the effluent of the existing treatment plant of the OID. A combined wastewater treatment system including chemical precipitation and ion exchange was used for the study. Following conclusions could be drawn from the study:

- As a result of the experimental studies to determine the optimum operational conditions and to improve the performance characteristics of the treatment units, it was found that more than 90% SS and fecal coliform removal was achieved with chemical precipitation. Sludge was mainly originated from $Ca(OH)_2$ and TSS precipitations. The sludge from the BOID has been disposed in IZAYDAŞ (İzmit Waste and Residue Treatment Incineration and Recycling Co. Inc.). Optimum removal efficiency was obtained by using $Ca(OH)_2$ at pH 11 in the chemical precipitation process. SS which prevent the efficient operation of ion exchange resin processes as stated by [42], were removed with a rate of 96% at the chemical precipitation process. Similarly, heavy metal removal efficiency was obtained above 90% with chemical precipitation by using $Ca(OH)_2$ at pH 11 [43]. Lin et al. [23] took the standard value of the conductivity parameter as 750 µS/cm and found the wastewater to be reusable in their research on the agricultural reusability of the wastewaters obtained from the treatment plant outlet of an OID in Taiwan. The standard value of 250 (µS/cm) was used for conductivity and a reusable water for agricultural irrigation purposes with a better quality than [23] reported was obtained in the study reported here.

- The wastewater quality after the ion exchange process met the legal agricultural irrigation water standards, and therefore it can be concluded that the wastewaters of the OID could be reused for agricultural irrigation purposes.
- The effluent from the WWTP of the OID is categorized as 5th class (worst) according to the agricultural irrigation water standards defined in Turkish WPCL [34]. After the application of the combined wastewater treatment system in this study, the quality of the wastewaters of the OID increased up to 1st class (best), and it was found that the water with this quality could be reused for agricultural irrigation purposes.
- It has been determined that faecal coliform can be classified as 3rd class (usable irrigation water) by means of chemical precipitation in accordance with the agricultural irrigation water standards specified in Turkish WPCL [34].
- In the model that [44] reported for the water reuse potential in European countries, Turkey is in the 4th order of 31 countries in the year 2025 projection. Considering the rapid loss and pollution of the water resources in the forthcoming years, the wastewater reclamation and reuse plants for the organized industrial districts, which are significant threats for the water sources with the quantity of the waters they consume and with the pollution they generate, would be essential for a sustainable water policy.

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