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The characterization and analysis of chemical contaminations of pharmaceutical industrial wastewater (case study: North of Iran)

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Abstract

This study describes a general risk-assessment and treatment approach to determine acceptable level of contaminant concentrations in the wastewater of pharmaceutical company. For definition chemical contaminants at studied company, it has reviewed available data on materials that company consumed annual. As a result, it was indicated high levels of formaldehyde, cyanide and some other heavy metals. Physicochemical parameters in liquid effluents of pharmaceutical company were determined in both chemical laboratory and open wastewater effluent channel. The paper offered a pre-treatment before traditional industrial wastewater treatment. This paper proposes a pre-treatment procedure to be applied before the traditional industrial wastewater treatment. In addition, heavy metals and cyanide in chemical laboratory are discretely removed by chemical treatment methods. It may provide effective to apply the combination of biological treatment of carbon and nutrient removal for final wastewater treatment in order to discharging to surface waters.

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Introduction

In recent years, there have been growing concerns on the active pharmaceutical ingredients, solvents, intermediates and raw materials that could be present in water and wastewater including pharmaceutical industry wastewater (Addamo *et al.*, 2005; Andreozzi *et al.*, 2005). Bulk pharmaceuticals are manufactured using a variety of processes including chemical synthesis, fermentation, extraction, and other complex methods. Moreover, the pharmaceutical industry produces many products using different kinds of raw material as well as processes; hence it is difficult to generalize its classification (Kolpin *et al.*, 2002).

Pharmaceutical effluents, wastes and emissions, contain toxic and hazardous substances most of which can be detrimental to human health. One of the most significant current materials in this type of effluent is heavy metals such as Cd, Co, Hg, Pb, etc. and cyanide (Onesios *et al.*, 2009). Heavy metals define as any metallic chemical element that has a high density and is poisonous at lower concentration (Yadav *et al.*, 2013). Cyanide is included in the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) priority list of hazardous substances (EPA, 1991) and it occupies 28th position in the list of most hazardous chemicals (Naveen *et al.*, 2014). Metal contamination from pharmaceutical industries comes from various sources. Some metals involved in such industries are: K, Mg, Ca, and Hg in the productions which are used in laboratories as reagents. Metal catalysts are other sources of metal contaminants (Adeyeye *et al.*, 2007).

Most of the literature published to date has been on the treatment of municipal wastewater (Mišík *et al.*, 2011; Klamerth *et al.*, 2012). However, there is a growing body of research that looks at the presence of active pharmaceutical ingredients in industrial wastewater, the treatment of these wastewaters and the removal rates (Deegan *et al.*, 2011). Traditional wastewater treatment methods as activated sludge are not sufficient for the complete removal of active pharmaceutical ingredients and other constituents from these waters.

Wastewater reuse has emerged as an important and viable means of supplementing dwindling water supplies in a large number of regions throughout the world. In many instances, reuse is also promoted as a means of limiting wastewater discharges to aquatic environments (Stackelberg *et al.*, 2004; Drewes *et al.*, 1999). Conversely, guidelines pertaining to chemical contaminants are typically limited to bulk parameters such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), pH and total suspended solids (TSS) (Weber *et al.*, 2006). In many situations these simple parameters provide suitable surrogate indications of the likely presence of chemical species of concern. This situation is now on the very verge of change as scientists and regulators are grappling with how best to address the issues presented by a wide range of individual chemical contaminants.

The paper takes the form of a case-study of the pharmaceutical industry of environmental risk assessment of chemical contaminations in the industrial area of Rasht, Iran. The present work evaluated the concentration of heavy metals and other contaminations in the wastewater effluent and its environment in a pharmaceutical industry. This type of work is necessary to alert the hazards it exposes to if such effluents are released to the water without treatment and more so when designing appropriate systems for wastewater treatment when releasing to surface water.

Material and methods

a) Studied area

The liquid effluents samples were collected from pharmaceutical company located in the industrial area of City of Rasht in Gilan province, north of Iran (Fig. 1). The amounts of heavy metal were calculated with data being gathered via pharmaceutical company data based on the annual consumption of compounds containing heavy metals.

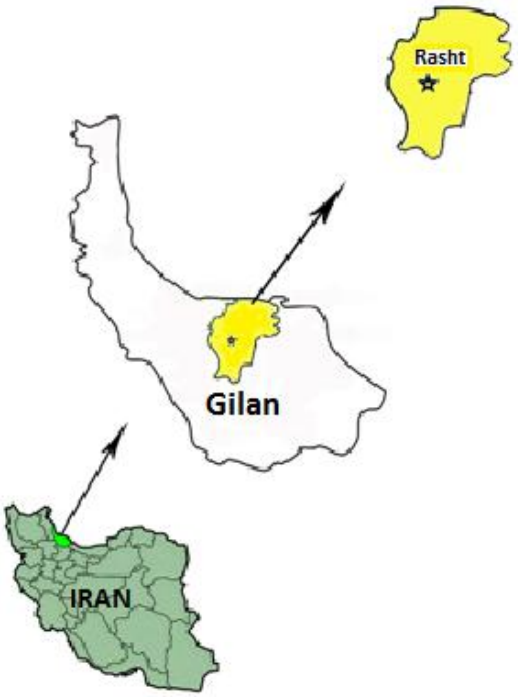

Fig. 1. Situation of Studied area.

b) Sampling procedure and treatment

The first set of samples was collected from the manhole close to the chemical laboratory where liquid wastes generated were generally discharged. The second set of samples was collected from the open output effluent channel where all the effluent of company was discharged in (final effluent).

Collections were done on the two different days. Liquid samples were collected into clean 1-litre rubber containers. Sample collections were done in every 30 min. The liquid effluent samples' temperatures and pH were taken immediately at the site of collection. The liquid samples were stored in the deep freezer until analyses were carried out.

c) Physico-chemical analysis

Temperature was measured using a simple thermometer calibrated in 0˚C. pH was measured with indicator paper (Macherey-Nagel, Germany). The H_2SO_4 (98%, Merck Company) were added in order to fix the samples below pH 2 for measuring COD, TP, N-nitrate, N-ammonium, oil and grease. The HNO_3 (65%, Merck Company) was added for preparing heavy metal samples. For analysis the BOD, ortho-P and N-nitrate measurements needed no fixation. The sample poured into labeled bottle containers. Then samples were sent to water and wastewater laboratory. The analyses were carried out according to the standard methods (APHA, 2005).

Results and discussion

This company has been providing a large proportion of small volume parenteral dosage form needs for health care system in Iran. Apart from ampoule, which is its main focused dosage form, semisolids (cream, ointment, gel and suppository), oral liquids and syrups are fully operational. Production at this plant is adjusted to meet the seasonal demand for many of these products. Thus, wastewater characteristics vary during the year and the week. In the pharmaceutical production unit, there are phase I including units of manufactured ampoules, filter, autoclave and filling ampoules, and phase II including medicinal ointments and gels, making the syrup, filling the syrup, making suppositories. In order to manufacturing of the products, the various vessels and mixers with different volumes are used. The industrial wastewater resulted from washing these vessels in each unit, are entered to specified sewage collection systems.

a) Physicochemical parameters

Both temperature and pH in the direct manhole of chemical laboratory were slightly lower than the corresponding values in the open output effluent channel. Temperature (˚C) was 31.0 in open effluent channel but 28.0 in manhole of chemical laboratory; also the pH was 6-7 in both. The physicochemical analysis data of chemical laboratory and final wastewater effluents and their limitations are presented in Table 1.

b) Microbiology Laboratory

The Microbiology Laboratory of this company carried out different microbial tests. The existing contaminants in the wastewater effluent of microbial laboratory are included Deconex and Savlon (50

g/day) as disinfection, NA, TSA, SDA and LB medium (650 g/day).

Table 1. Effluent analysis of the pharmaceutical wastewater.

Parameter	Chemical Laboratory wastewater (mg L^{-1})	final wastewater effluent (mg L^{-1})	Effluent Limitations (mg L^{-1})
COD	373	329	60 (moment 100)
BOD_5	160	131	30 (moment 50)
Ortho-P	1.2	0.04	6
TP	2	2.2	-
N-nitrite(NO_2)	3.1	2.1	10
N-nitrate (NO_3)	5	4.6	50
N-ammonium(NH_4)	2.5	3.5	2.5
Oil & Grease	-	26	10
pH	6.5	7	6-9
Temperature	28	31	-
Cr	trace	trace	Cr^{+6}:0.5, Cr^{+3}: 2
Cd	trace	trace	0.1
Fe	1.2	1.1	3
Cu	0.2	0.1	1
Pb	0.03	trace	1
Ni	trace	trace	2

The ratio of COD/BOD resulting of different tests showed the concentrations of these compounds in finished wastewater generally were similar to or less than concentrations in the effluent limitations therefore it can be concluded that the disinfectant entering effluent via microbiology lab will have no impact on the biological treatment hence, the microbiology laboratory wastewater requires no treatment.

c) Chemical laboratory

A wide range of chemical contaminants have been in chemical laboratory effluent that persist in conventional treatment processes. The heavy metals concentrations of plant effluents were calculated based on the annual consumption because of the production program of company vary according to seasonal demand. The data is given in Table 2. These include inorganic compounds, heavy metals and complex-forming compounds. Many of these chemicals are known or suspected of deleterious implications to human health or the environment.

The major metals that were of high concentration were Ag, As and cyanide compound. Following the trail of high concentration values among the trace metals were Zn, Pb, Hg and Mo in the samples as enumerated for major metals.

d) Fumigation System

Formaldehyde gas is employed for fumigation system in different units every week. This operation is carried out by mixing potassium permanganate and formalin solution for 18-24 hr (Ackland *et al.*, 1980). The remaining materials are poured into the wastewater after filtering. The annual consumption of formalin is 4 liters and potassium permanganate is 5 kg.

Due to the different amount of water used for washing, formaldehyde levels in this area are 3300 to 5000 mM equal to 100000 to 150000 ppm. If formaldehyde directly discharges to wastewater, the final concentration will be 60 to 80 ppm. Considering that the formaldehyde minimal inhibitory concentration of bacteria is about 2.5mM to 75 ppm, so the concentration of formaldehyde in the final effluent is harmful for biological treatment (Sondossi *et al.*, 1989).

Table 2. The Calculation of peak values of effluent heavy metals based on annual consumption.

Heavy metals	Annual consumption (gr)	Approximately concentration in chemical laboratory effluent (mg L^{-1})	Approximately concentration in final effluent (mg L^{-1})	Effluent Limitations into surface water (mg L^{-1})
Zn	65.2	7.24	1.42	2
Ti	3.8	0.43	0.08	
Sn	9.1	1	0.19	10
Ag	110.5	12.27	2.3	1
Se	0.6	0.07	0.013	1
Ni	1.2	0.13	0.03	2
Hg	35.2	4	0.77	Slightly
Mg	0.07	0.007	0.002	1
Pb	33.6	3.73	0.7	1
Fe	40.9	4.5	1.2	3
Cu	3.2	0.35	0.2	1
Co	9.9	1.1	0.2	1
Cr	9.6	1.07	0.2	Cr^{+6}:0.5, Cr^{+3}: 2
Cd	1	0.1	0.02	0.1
As	68.1	7.6	1.4	0.1
Mo	1.6	0.18	0.035	0.01
V	8.7	0.97	0.18	0.1
Cyanide	128.5	14.28	2.5	0.5

e) Treatment Methods

There are various methodologies for wastewater treatment. It is important to select a proper treatment method according to the characteristics of wastewater.

The pharmaceutical industry employs a wide array of wastewater treatment and disposal methods (Struzeski *et al*., 1980). Wastes generated from these industries vary not only in composition but also in magnitude (volume) by plant, season, and even time, depending on the raw materials and the processes used in manufacturing of various pharmaceuticals. Hence, it is very difficult to specify a particular treatment system for such a diversified pharmaceutical industry. Many alternative treatment processes are available to deal with the wide array of waste produced from this industry, but they are specific to the type of industry and associated wastes. Available treatment processes include the activated sludge process, trickling filtration, the powdered activated carbon-fed activated sludge process, and the anaerobic hybrid reactor. An incomplete listing of other treatments includes incineration, anaerobic filters, oxidation ponds, sludge stabilization, and deep well injection. Based upon extensive experience with waste treatment across the industry, a listing of the available treatments and disposals is summarized at Table 3 (Struzeski *et al*., 1980).

Advantages of biological treatment for pharmaceutical wastewater are included good treatment efficiency, addition of extra chemicals not required, less sludge production and relatively much more economical.

Table 3. Different Type of Pharmaceutical Wastewater Treatment Methods and Their Efficiencies.

Types of treatment processes	Reduction in BOD (%)
Aerobic treatment – Activated sludge – Aerobic fixed growth systems	56 – 96
Anaerobic digestion with controlled aeration	80
Anaerobic digestion	60 - 90
Trickling filters	60 -98
Biofiltration (consist of aerator, clarifier & filters)	>90
Advanced Biological Treatment (provide, ammonia reduction & nitrification also)	90

f) Recommended method for this case study

According to above results, the most important chemicals in this wastewater are formaldehyde and heavy metals. The direct discharges of this waste can

threaten life in the surface water and groundwater resources. It is very important to find the practical way to degrade the organic and inorganic contaminants and reduce the toxicity of formalin wastewater. Due to its mutagenic and carcinogenic effects, discharging of formaldehyde-rich wastewater into the other wastewater without pretreatment may cause microbial activity inhibition in biological processes. Therefore, removal of formalin from wastewater are suggested to be separated from the main path of wastewater and treated separately. In order to reduce the toxicity of formaldehyde, it can be reacted with sodium sulfite. The reaction product is sodium formaldehyde bisulfate that not only is not toxic to microorganisms bus also is a biodegradable material (Tchobanoglous *et al*., 2005). After that, the wastewater can be treated by biological method. Furthermore, for removal of heavy metals from chemical laboratory wastewater, it can be successful to treat discretely by chemical methods. It was decided that the best method to adopt for this investigation was to increasing the hydroxide concentration by increasing the pH solution before they are discharged. It may be effective to apply the combination of biological treatment of carbon and nutrient removal for total wastewater treatment before discharging to surface water bodies (Heberer, 2004; Abou-Elela *et al*., 2008). It may provide effective to apply the combination of biological treatment of carbon and nutrient removal for total wastewater treatment in order to discharging to surface waters.

Conclusions

This study set out to determine the chemical wastewater of a pharmaceutical industry. The results depicted that wastewater effluent showed high levels of some heavy metals, cyanide and formaldehyde. The direct discharges of this wastewater can threaten life in the surface water and groundwater resources. Based on extensive study in treatment of pharmaceutical wastewater, the following specific conclusions may be drawn: Pretreatment of formaldehyde and chemical laboratory wastewater is advisable. The total waste stream should be treated by the combination methods of carbon and nutrient removal due to discharge into surface water resources. However, the substances synthesized by pharmaceutical industries are organic chemicals that are structurally complex and resistant to biological degradation, with assumption of appropriate methodologies for separation and pretreatment and selection of proper waste treatment, it can be possible to discharge this pharmaceutical wastewater in the receiving water such as surface water.

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