Determination of Methamphetamine, Cocaine, Morphine, and Codeine Rates in Urban Sewage through Gas Chromatography

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Abstract

Objective: In addition to damage to individual and social health, drug abuse can seriously endanger the aquatic environment through access to aquatic ecosystems. In this research, narcotic drugs (methamphetamine, cocaine, morphine, and codeine) in the input and output wastewater, the sludge arising from wastewater treatment in the wastewater treatment plant of Tehran municipality, and the output effluent in one of the hospitals in Tehran (Tehranpars Hospital) have been examined via GC gas chromatography and Solid Phase Micro Extraction. Method: Solid-phase micro-extraction is an equilibrium extraction method through which it is possible to use pollutants in low concentrations and with high sensitivity without using solvents by means of a proper calibration method. Gas chromatography is the analyzer, initially used with SPME, and, to date, many of its applications are based on separation and analysis by this device. Results: The results of this study showed that high concentrations of codeine and morphine exist in urban sewage and the efficacy of treatment plants in removing these contaminants was not significant (elimination percentages were 23% and 43%, respectively). It has also been observed that there is no cocaine in the study samples. Conclusion: The findings of this study have health-medical implications and points.

Keywords: narcotic drugs, solid phase micro-extraction, gas chromatography, hospital wastewater

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Introduction

Water pollution is defined as the increase in the amount of each factor as to physical, chemical and biological that changes water properties and its essential role in the specific uses. According to estimates from the United States Environmental Protection Agency (US EPA) about one-third of the world's waters are polluted, and the principle of water quality maintenance has been disrupted. The major causes of water pollution are: oxygen waste recipients, pathogens, plant nutrients, synthesized organic compounds, petroleum, inorganic chemicals (including drugs residual), minerals, sediment, radioactive substances (radiation) and heat. Water contaminating agents are very diverse and can pollute both groundwater and surface water. Groundwater contaminating agents include: minerals in surface mines, urban wastewater discharges and radioactive waste.

The water needed by human being typically consists of surface water and underground water, and if these resources are contaminated, human societies are endangered greatly. Today, with the growth of the population on the one hand, and water contamination and contaminated waste, on the other hand, it is of great importance to study and monitor different types of pollution in aquatic environment. Also, due to water shortage, we can reduce low-water crises through recycling and water refinery. In this regard, the quantities of pollutants must be evaluated before and after the purification. One of the pollutants that can enter the water basins through contaminated waterways, especially urban and hospital wastewater is chemical compounds of family of drugs. Considering the use of drugs and illegal drugs in the society as well as their disposal into the urban sewage system, one can provide useful information about their use in the society, the rate and the entry of these substances into the environment and water resources. Sewage pollution is mostly due to the presence of organic matter. The organic materials in sewage is unstable and can be converted into nitrites, nitrates and phosphates with aeration and oxidation, and then they are separated as deposited substances from sewage and this is the aim of establishing sewage treatment plants in cities. In order to show the degree of sewage contamination, the amount of oxygen required to oxidize the material is usually measured instead of measuring the rate of organic material in the sewage. The bacteria in the sewage that are beneficial in treatment process include aerobic and anaerobic bacteria.

Drugs are chemical compounds which change the level of consciousness and brain function when used. The main target of drugs is the brain. There are some receptors in the brain that are affected by these substances. These receptors are divided into 3 groups: First group, which regulates and relieves pain, reduces the activity of the respiratory center, constipation, and addiction; second group: the effect on second recipients reduces pain and increases urine volume; third group: the effect of the drug on the third group receptors reduces pain. Generally, drugs are divided into three categories: 1) Opiates: These substances affect the central nervous system and slow down physical and mental activity in the individual, substances including heroin, methadone, pethidine, and various types of tranquillisers .; 2) STIMULANTS: these substances also affect the central nervous system; increase the level of emotion, physical and mental performance in the drug user. Its synthetic types also include amphetamines and their derivatives and barbiturates. 3) HALLUCINOGENS: These substances disrupt the mental and physical activity of the individual and cause disillusion, by creating complex effects on the central nervous system.

Morphine: Morphine is one of the most important alkaloids. Alkaloids are referred to as any organic chemical compounds that have at least one nitrogen atom in the heterocyclic ring. Using morphine in the present form has been prevalent to relieve pain (sedative and painkiller of severe pains) since the 19th century, and in terms of pharmacological classification, it weakens the central nervous system (from poppy to ecstasy, Kashi , Counter Narcotics Police, 2015). The presentation of the chemical structure and morphine features are presented in Figure 1.

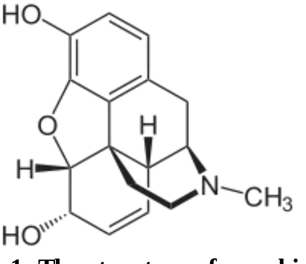

Figure 1: The structure of morphine

Codeine: Codeine is an agonist drug that is often seen as white crystalline and is considered as a sedative and analgesic component of narcotic drugs and opiate derivatives, and is made at the concentration of 10.1% to 2%. Codeine is available in various pharmaceutical products. This drug is delivered in three ways including oral (pill, capsule, and syrup) anal (suppository) and injection (subcutaneous and muscular). The oral form of codeine is most often formulated as codeine hydrochloride and codeine sulfate. The chemical structure and codeine characteristics are presented in Figure 2.

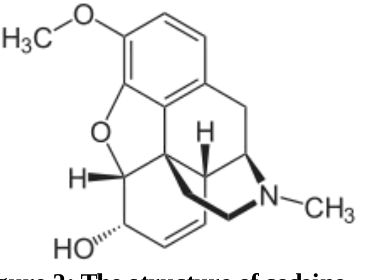

Figure 2: The structure of codeine

Cocaine: The chemical composition of cocaine is also a benzoylmethylecgonine compound that is a member of the atropine family and is a plasma mediator, which inhibits neuronal conduction and stimulates the central nervous system. Cocaine is in psychedelics group. The chemical structure and characteristics of cocaine are presented in Figure 3.

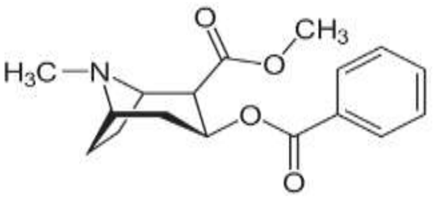

Figure 3: The structure of cocaine

Methamphetamine: Methamphetamine is a potent central nervous system stimulant. With direct effect on the mechanisms of brain, it creates excitement in the individual. Methamphetamine also causes severe sleep disorder or severe insomnia. The methamphetamine user suffers from severe appetite loss and cannot eat for hours or even days. This substance is in the form of crystalline glass, odorless and bitter, which is easily found in alcoholic and non-alcoholic beverages.

The chemical structure and methamphetamine features are presented in Figure 4.

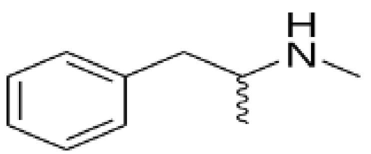

Figure 4: The structure of Methamphetamine

The purpose of this study was to examine narcotic drugs (methamphetamine, cocaine, morphine, and codeine) in the input and output wastewater, the sludge arising from wastewater treatment in the wastewater treatment plant of Tehran Shahid Mahalati, and the output effluent in one of the hospitals in Tehran (Tehranpars Hospital).

Method

Population, sample and sampling method

The main method of the research was based on an analytical study. The samples were taken from the input and output wastewater, the sludge arising from wastewater treatment in the wastewater treatment plant of Tehran Shahid Mahalati, and the output effluent in one of the hospitals in Tehran (Tehranpars Hospital) in fall 2015. In this research, for sampling, glass and plastic polyethylene containers (one liter and four- liter) were used. In order to maintain the samples and transfer to the laboratory, they should be stabilized. There is a certain method to fix each factor. Solid-phase micro-extraction is an equilibrium extraction method through which it is possible to use pollutants in low concentrations and with high sensitivity without using solvents by means of a proper calibration method. Gas chromatography is the analyzer, initially used with SPME, and, to date, many of its applications are based on separation and analysis by this device.

In this research, gas chromatography was used with solid-phase micro-extraction for data analysis. A new method was developed for the complete injection of high-boiling compounds into the gas chromatography system based on optical fibers. Thus, an optical fiber was impregnated with the test specimen and after evaporation of the solvent, it was transferred to the injection valve, and then by passing the laser beam through the optical fiber, the adsorbed analyte in the fiber surface was desorbed by laser method and entered the chromatographic column (Jiang et al., 2009). After the sampling (250 milliliters for each sample), of the influent waste water and treated wastewater, as well as the return activated sludge, the samples were stabilized according to the existing methods in order to maintain the samples and transfer to the laboratory and were transferred to the laboratory. The specimens were stored in dark containers and were tested up for three days after sampling. All experiments were performed according to the standard APHA (2001) method. At the end, each set of tests was repeated 3 times to control their errors. It is worth noting that the parameters were measured in ng / lit. Before performing the extraction operation, samples were passed from filter paper of "*man what*" model and were prepared for extraction. To extract narcotic compounds in this study from obtained sewage and sludge samples, first extraction syringe was filled with 5 ml of methanol and then washed with 5 ml of distilled water. To perform solid phase micro-extraction, a small volume (250 ml) of extraction phase with high temperature tolerance adhesives was stuck in the small stainless tube, the end of which should extend to the syringe needle. The coated fiber was immersed in the solution for a specific time (2 to 15 minutes, in this study, 10 minutes). At this stage, the sample was absorbed into the fiber, then the fiber was returned to the SPME syringe and the needle was removed from the sample container. In the next step, the needle containing the extracted analyte was injected into the input of gas chromatography device. The effect of the sample pH parameter on the recovery rate in the extraction process has received much attention from various studies and in this study, PH = 3 was selected.

Findings

The analysis of the influent and effluent samples (treated) from the wastewater treatment plant is presented in Table 1. The concentration of the narcotic drugs studied in this research is in ng / g per liter of the sample. These tables show the rate of each of the opioids examined in the influent and effluent sewage and the excess biological sludge extracted from urban wastewater treatment.

Table 1: Concentration of the Pollutants Studied in the Influent Samples of Urban Wastewater Treatment Plant by Type of Test

Drugs		*Influent sewage sample (ng/L)*					*Influent sewage sample (ng/L)*	
		Sample (1)	*Sampl (2)*	*Sample (3)*	*Sample (4)*	*Sampl (5)e*	*Mean*	*Number of studied samples*
codeine	**Influent sample**	80	12	57.5	101	150	80/1	5
	Affluent sample	3/1	24	10/4	197	76		
morphine	**Influent sample**	24/5	27	15	187	53	61/3	5
	Affluent sample	11	13	26	11	83/5		
cocaine								5
methamp hetamine	**Influent sample**	11	5	47	97	90	50	5
	Affluent sample	4/7	31	80	5.8	101		

The diagram of the comparison of the average concentration of pollutants studied in the influent and affluent sewage samples is presented in Chart 1.

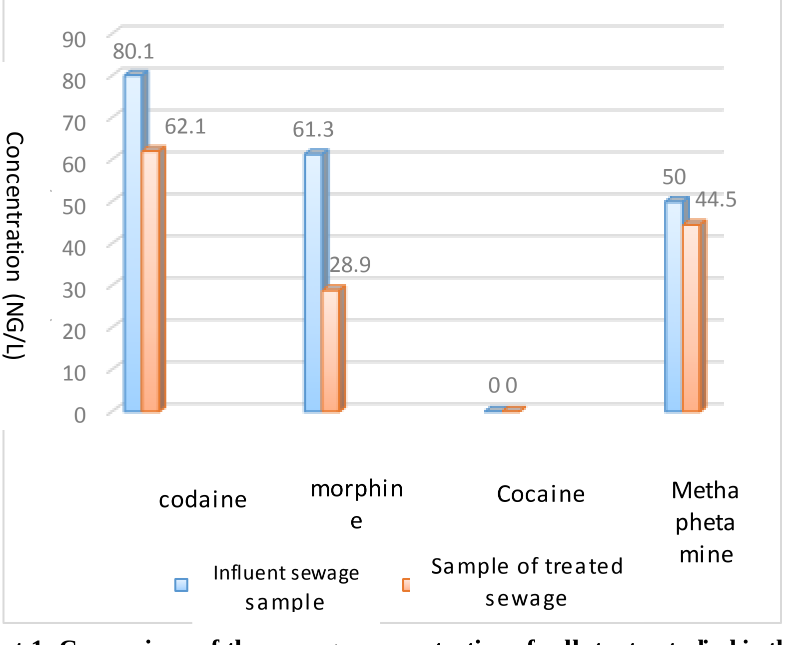

Chart 1: Comparison of the average concentration of pollutants studied in the influent and affluent sewage samples

According to Table 1 and Figure 1, the efficiency of the wastewater treatment plant is observed in removing or changing the nature of the pollutants under investigation. The treatment of sewage is always along with the production of two distinct parts of wastewater and sludge. The number of samples tested in each experiment was repeated three times. The chart of the comparison of the average concentrations of pollutants studied in biological surplus sludge samples is presented in Figure 2.

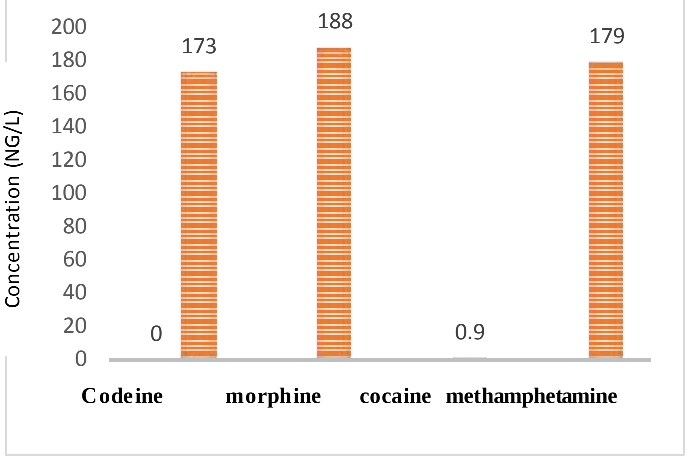

Chart 2: Comparison of the average concentration of pollutants studied in surplus biological sludge samples

The concentration of narcotics in surplus biological sludge of urban wastewater treatment plant in by the type of material and sample number is presented in Table 2. It should be noted that the concentration of the drugs studied is in nano grams per liter.

Table 2: Concentration of Narcotic Drugs of Surplus Biological Sludge of Urban Wastewater Treatment Plant In terms of Substance Type and Sample Number

Sample number	*Codeine concentration*	*Methamphetamine concentration*	*Morphine concentration*	*Cocaine concentration*
1	70	191	199.5	0/65
2	287	247	61	0/60
3	380	168/3	68	1
4	113	38/7	81/5	0/75
5	15/1	250	530	1/5
Average	173	179	188	0/90

The concentration of narcotics in sewage samples of Tehranpars Hospital by type of material and sample number is presented in Table 3. It should be noted that the concentration of the drugs studied in this study is in nano grams per liter.

Table 3: Concentration of Drugs in Sewage Samples of Tehranpars Hospital by type of Substance and Sample Number

Sample number	*Codeine concentration*	*Methamphetamine concentration*	*Morphine concentration*	*Cocaine concentration*
1	73/2	3/2	161/3	13
2	41	6//3	101/2	37
3	300/3	1/8	568	51
4	373	1	90	19/3
5	170	1/2	84/5	64/7
Average	191/5	2/7	201	37

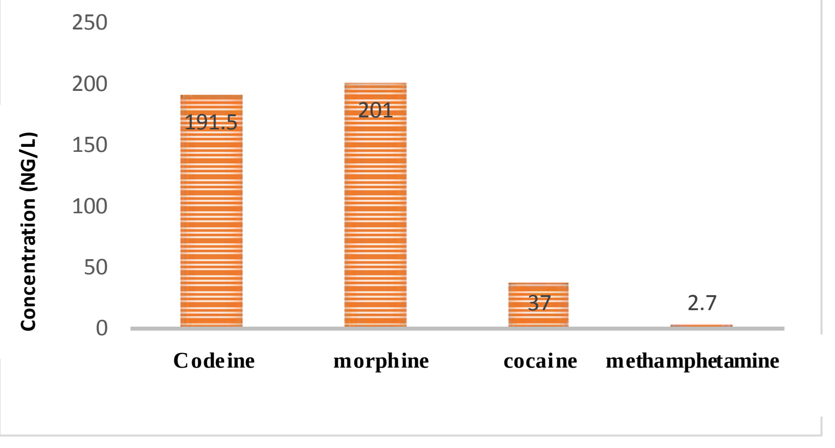

Chart 3: Comparison of the average concentration of pollutants studied in the samples taken from the hospital wastewater

As shown in Chart 3, in the samples taken from the sewage produced in the hospital, all the narcotics examined in this study have different concentrations. In the hospital wastewater, morphine has the highest average concentration (201 ng / l).

The average flow rate of the influent wastewater of the Shahid Mahalati Wastewater Treatment Plant is 200 cubic meters per hour and the population of this wastewater project was 30,000. Table 4 shows the average estimate of drug use in this study.

Table 4: Estimated Average Drug Use

Drugs	*Influent sludge of wastewater treatment plant*		
	Range	*Average value*	*Average consumption (mg/day 1000 inh)*
Codeine	12-150	.180	385.0
Morphine	25-287	3.61	2940.
Cocaine	-	-	-
Methamphetamine	5-97	50	240.

As you can see, the highest use is dedicated to codeine with 0.385 mg per day per 1000 inhabitants. The use of opioids is in practice several times more than the estimated results, but as the exact figures are not available for the population covered by this wastewater treatment plant, we only relied on this value.

Discussion and Conclusion

Wastewater treatment is carrying out any physical, chemical, biological operation or combining them on raw sewage to reduce or eliminate any pollution from the sewage system and to increase the quality of the waste water to the standards required to dispose the wastewater from the environment. In order to prevent the destruction of biological resources, it is necessary to prevent the disposal of untreated sewage containing pollutants such as residues of drugs and other pollutants into the environment. Also, the use of treated waste water for agriculture in our country due to shortage of rainfall can compensate for a part of the water requirement and also due to the existence of nutrients required by the plant in wastewater for the purpose of fertilizer consumption can be also economical. The results of this study indicate that high concentrations of codeine and morphine were in municipal sewage sludge and the efficacy of the treatment plant in removing these pollutants is not significant (removal percentage is 23 and 43% respectively). It has also been observed that there is no cocaine in all of the samples. Morphine, codeine, methadone, and EDDP are present at the highest concentration in comparison with other opioids. Tehran has around 150 hospitals, 8% of which lack a sewage treatment system, and 34% of which have defective wastewater refinement plants. The presence of drug compounds and especially opiates in water resources is usually a proportion of the wastes resulting from the pharmaceutical industry, personal hygiene products, hospital and therapeutic drugs; and drug abuse in addicts. the majority of sewage treatment plants can only eliminate a very low percentage of opiates and the remaining will directly enter the receiving waters; Therefore, it is necessary to use more efficient and effective methods to remove these pollutants.

Also, the results of this study showed that the use of solid phase micro extraction method by gas chromatography as a more sensitive method, which can be performed in Iran, has led to the detection of very small amounts of narcotics in existing samples, and this is similar to that of other research in 2015, by Gago and Ferro as a new method to determine the rate of 148 substances, including drug residual, as well as narcotics in sludge from sewage treatment. In another study by Samadi and Bani Assad in 2011, by combining solvent liquid-liquid activated carbon and micro-extraction, a new method was carried out for measuring n-methylpyrrolidine in different matrices. In another study, Sarafrazizadi and Raufi Nejad as in the present study, applied gas chromatography and sample preparation using *directly* suspended droplet microextraction (DSDME) in measuring two antidepressants and three cephalosporin drugs. Those results were reported with high precision for small amounts of drug substances. The disposal of drugs into surface water can lead to pollution and has irreversible risks to consumers. According to the measurements, the concentration of the contaminated pollutants and the frequency of them in the studied wastewater are as follows:

1) Codeine: The concentration of codeine pollutant decreases from 80 ng / lit to only 62.1 ng / liter (equivalent to 22.5% removal). In addition, the results show that in tested samples, there was a higher concentration of codeine than other opiate drugs that could be due to the drug's use spectrum in the painkillers used by individuals and the disposal of waste water effluent.

2) Morphine: The concentration of morphine pollutant decreases from 61.3 ng / lit to 28.9 ng / liter (equivalent to 53% removal). Existence of a significant amount of morphine in sewage was due to direct substance abuse because, as previously stated, morphine is excreted through the urine and bile of the drug user.

3) Methamphetamine: The concentration of methamphetamine pollutant decreases from 50 ng / L to 44.5 ng / L (equivalent to 11% removal). The highest removal percentage was related to morphine (53%) and the lowest removal percentage was dedicated to methamphetamine (11%). In the study, the rate of narcotics and their metabolites in sewage was monitored and in the influent and effluent sludge from 15 wastewater treatment plants, 8 compounds of the 11 compounds were investigated and most of the samples have been containing codeine, morphine, EDP and methadone, which is similar to the present study (Baselt, 2004).

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