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Advanced Method of Detection of Adulterants Present in Alkaloids by R & D and Waste Water Treatment by ETP

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Abstract: **Today's adulteration detection in drugs make a challenging for the researcher. The latest techniques are available but they are costlier which may effects the price of generic and other drugs and also make a sharp impact on environment. The demand of alkaloids by different pharma industries to make life saving drugs and for research purposes has increase now a days. The adulteration is done with in the raw material increases just to for increase the quantity of the raw material for money making purpose.Sometimes the opium purchased from outside is adulterated with small amounts of horlicks / bournvita and milk powder which is difficult to detect, hence R&D of this factory develop its own method for detection of these adulterants using TLC separation. In the above study extraction of various alkaloids mainly the extraction of morphine sulphate from opium as % content of morphine in opium is highest i.e ~12% and its medicinal importance in daily life and the detection of impurities by measuring COD, DO, TDS, TSS &TS of water sample and also the removal of impurities from the waste water of synthesized alkaloids by using (ETP) effluent treatment plant to make them alkaloid free water which may effects ecological balance. The ETP treat water to such an extent that it can be used for all purpose except cooking and drinking. The above experimental work which I did under summer training program for that I chose Government of India's opium and alkaloid factory situated in Ghazipur, Uttar Pradesh.**

Keywords: **Opium, Effluent treatment plant, TLC, COD, DO, TDS, TSS, TS**

1. INTRODUCTION

Factory visited during summer training is GOVERNMENT OPIUM & ALKALOID WORKS situated in GHAZIPUR, Ghazipur is well known all around world for Asia's second largest government opium factory. It is one of the tow factory in country which chiefly produces different alkaloid products, specializes in manufacture of alkaloid and export opium. The raw material used is raw opium which is derived from the poppy plant. Opium is the latex obtained by incision from the unripe capsules of **Papaver Somniferum**, an annual plant. Only pod portion of the plant can produce opium alkaloids, these pod called seed pods, capsules or either oblate. The plant is dried by heat or spontaneous evaporation and worked into somewhat irregularly shaped masses, it is known as INDIAN OPIUM and it contains not less than 9.5% of morphine. Poppy or plant seeds apart from being used as planting seeds are also use to produce cooking oils, pats and perfume etc.

1.1 Products of this factory

1.1.1. Raw opium
1.1.2. Natural narcotics: Morphine sulphate, Codeine phosphate, Codeine sulphate, Thebaine, dionine etc
1.1.3. Semi-synthetic narcotics: Oxycodeone HCl, Dihydro-codeine bitartarate, Hydrocodone
1.1.4. Non-narcotics: Noscapine, Papaverine

1.2 Morphine as medicinal drug: Morphine,is a analgesic drug and the major psychoactive chemical in opium. It is known as the gold standard of analgesics in clinical medicine which is used to relieve intense pain**.** It acts directly on the central nervous system (CNS) to relieve pain like other alkaloids of opium. [1]]

Morphine is used as precursor in the manufacture of a large number of alkaloids such as heroin, codeine, dionine etc, which itself has a large family of semi-synthetic derivatives.

Medicinal uses of morphine:

1.2.1 Immediate release of morphine is beneficial for:-

- reduces the symptom of acute shortness of breath due to both cancer and non-cancer causes.
- the settling of breathlessness at rest or on minimal exertion from conditions such as advanced cancer or end-stage cardio-respiratory diseases.

1.2.2 Regular or low-dose sustained release morphine significantly helps in:[2]

reducing breathlessness safely, with its benefits maintained over time.

1.3 Classification of alkaloids:

1.3.1 Natural Narcotics: These act centrally and causes addiction, it produces CNS depression and has no anti-inflammatory effect.

e.g:Morphine sulphate, Morphine hydrochloride, Codeine phosphate, Codeine sulphate, Thebaine, Dionine.

1.3.2 Non-Narcotics: These act peripherally and do not causes addiction, it does not produces CNS depression and has anti-inflammatory effect.

e.g Noscapine, Papaverine

1.3.3 Semi-synthetic Narcotics:

The narcotic drugs that cause the most addictions are the semi-synthetics:e.gheroin, hydromorphone, oxycodone, and hydrocodone.

Table: 1. Details of some alkaloid products of opium [3]

Name of drug	Morphine sulphate	Noscopine	Dionine[ethyl morhine hydrochloride]	Codeine phosphate
Formula	(C17H19NO3)2, H2SO4,5 H_2O	C22H23NO7	C19H23NO3,HCl,2 H_2O	C18H21NO3,H3PO4,1/2 H_2O
Category	Narcotic, Analgesic	Anti-tussive	Narcotic, Analgesic	Analgesic, Anti-tussive
Description	Colorless, glistening needled, odorless and bitter in taste	Fine, almost white crystalline powder, odorless and tasteless.	Colorless, glistening needles or white crystalline powder, odorless and bitter in taste.	Fine, white, hexagonal prism, odorless and bitter in taste.
Solubility	Soluble in hot water, glycerine. Insoluble in ether and chloroform	Insoluble in water, freely soluble in chloroform	Soluble in water, alcohol. Insoluble in ether	Freely soluble in water, sparingly soluble in chloroform and ether.
M.wt	758.83 g	413.42 g	385.86 g	406.27 g
Dose	10 to 20 mg	15 to 30 mg	6 to 30 mg	10 to 60 mg
Storage	Well closed, light resistant container.	Well closed, light resistant container	Well closed, light resistant container	Well closed, light resistant container
Identification	sprinkle a small quantity in powder form on the surface of a drop of nitric acid---------- orange red color appears.	0.1 g in a small porcelain dish, add a few drops of sulphuric acid and stir------ greenish yellow color produced which upon warming becomes red------ turns violet	To 10 mg add 1ml of sulphuric acid and 0.05 ml of 1.3% solution of ferric chloride and treat on water bath-----blue color is produced which changes to red on addition of 0.05ml of nitric acid.	on surface of one drop of nitric acid, place a little sample------ yellow but not red color is produced. (distinction from morphine)

1.4 Waste water treatment:

The waste water discharge from the factory is termed as effluents. The problem of disposal of industrial water whether solid, liquid or gases and these three types of waste have the potential of ultimately polluting water. Effluent from an industry may carry a broad and variable range of contaminants including lime, cyanides, plasticizers, toxic acid, corrosive alkalies, oils, greases, suspended solids and thermal pollutants etc. The toxicity of various pollutant contaminate water system and are also poisonous for aquatic organisms. Most of the industrial effluents like are extremely lethal and waste like sulphuric acid waste from coal mine is a chronic pollution which enhances hardness of water and corrodes concrete as well as drastically affects the living organisms if release directly into rivers without treating it [4].In order to avoid water pollution and make use of water which is discharging from factory, the factory for waste water management has installed ETP (Effluent treatment plant). The ETP of GOVT.OPIUM & ALKALOID WORKS, GHAZIPUR started functioning at 30/10/1989. The main purpose to establish ETP is to release clean and fresh water into river from factory to avoid river pollution. The ETP treat water to such an extent that it can be used for all purpose except cooking and drinking.

1.4.1 The common stages of ETP (Effluent treatment plant) are:

1. Primary treatment [MECHANICAL TREATMENT]
2. Secondary treatment [BIOLOGICAL TREATMENT]
3. Tertiary treatment [ADVANCED TREATMENT]

1.4.2 Components of Effluent treatment plant: [6]

1.4.2.1 Screen: chamber, rectangular in shape. In it large size solid waste like paper, plastic, leaves etc. are removed then sewage enter in grit chamber.

1.4.2.2 Grit chamber {GC}: sewage sedimentation is split up into two stages namely:

i removal of inorganic solid in first stage
ii removal of organic solid in second stage

Organic content of sewage is termed as grit which is consists of sand, gravel, ash, clinckers, organic materials etc.

1.4.2.3 Equilization tank: In this tank mixing of effluent is done to make different characteristics of different effluent uniform. In this tank treated water is maintained a constant pH using growing bacteria and calcium hydroxide.

Effluent in tank posses: pH = 7.5-9.0
BOD = 100 -300 mg/l
COD = 200-1500 mg/l
T.S = 200-500 mg/l

1.4.2.4 Flocculation tank [FT]: Equilization tank effluent comes to this tank. When alum and effluent is thoroughly mixed in this tank it produces a thick insoluble gelatinous ppt called FLOC.

Floc ions are electrically charged i.e positive while all colloidal particles have negative charge therefore floc attracts the uniform colloidal particle and causes their removal easily by settlement at the bottom of tank, process is called flocculation.

$$Al_2(SO_4)_3 + 3\ Ca(HCO_3)_2 + 18\ H_2O \longrightarrow 2\ Al(OH)_3\downarrow + 3\ CaSO_4 + 18\ H_2O$$

In above reaction, calcium bicarbonate represents neutral alkalinity of water, some water do not have sufficient alkalinity, so calcium oxide is added which react with water to form calcium hydroxide.

1.4.2.5 Primary settling tank (PST): (Sedimentation tank)

The effluent from FT is fed into PST to settle down the solids present in waste water. Detention period is 3 hr. Depending upon the surface loading the BOD removal is 18-40% and suspended solid removal is about 40-90%.

The sludge formed at the bottom by gravitational settling is removed from PST by vacuum suction as underflow. The clear liquid produced is known as overflow and does not contain readily settle able matter.

1.4.2.6 Aeration tank: Treatment of sewage with bacteria is called secondary treatment which is most important stage in processing of sewage or industrial effluent because in primary treatment 30-35% BOD and 60% suspended solids are removed.

Objective: Stabilisation of organic matter which can be done either by aerobic or anaerobic bacteria. Generally fresh cow dung & DAP (Diammonium phosphate) is added in aerobic process.

Reaction: All these reactions take place in presence of bacteria.

$$\text{Organic-C} + O_2 \longrightarrow CO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (\text{i})$$
$$\text{Organic-H} + O_2 \longrightarrow H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (\text{ii})$$
$$\text{Organic-N} + O_2 \longrightarrow NO_3^- \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (\text{iv})$$
$$\text{Organic-S} + O_2 \longrightarrow SO_4^{2-} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (\text{v})$$
$$\text{Organic-P} + O_2 \longrightarrow PO_4^{3-} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (\text{vi})$$

1.4.2.7 Secondary settling tank (SST)

It is provided to maintain mass liquor suspended solids (MLSS) of the effluent and designed in such a way that it maintains flow of effluent 250 m3/day with detention time 2-3 hrs in suspended solids. The sludge finally beds with the help of sludge pumps.

1.4.2.8 Sludge drying beds:

Sludge is a byproduct of all effluent plant. With the help of ETP the purified water is separated and byproduct sludge is used as manure after drying due to its high fertility. There are 5 sludge beds in ETP of this factory.

- Sludge bed no. 1&2 receive sludge from PST.
- Sludge bed no. 3,4,5 receive sludge from SST.

1.5 Physio-chemical analysis of industrial effluents:

Table2: Analysis of inlet & outlet water samples of ETP plant [5]

Physical analysis	Chemical analysis
1]Color & odor	1]Total hardness: indicates water quality mainly in terms of calcium and magnesium. Analysis is done by complexometric titration. TOTALHARDNESS= TEMPORARY HARDNESS+ PERMANENT HARDNESS
2]Temperature 3]pH is measure of relative acidity or alkalinity of water. For pure water at 25ºC, pH= 7.	2]Calcium hardness:. Calcium occurs in water mainly is due to presence of limestone, dolomite etc. EDTA titrimetric method can be used for determination of calcium rapidly.

pH = -log[H+]	
4] Total dissolved solids (TDS) = (wt. of dish with sample residue after dryness – empty wt. of dish) x 10^6 / Volume of sample taken. (mg/l)	3]Magnesium hardness :Mg salts occur in natural water, sea water ~ 130 ppm =(Total hardness-Calcium hardness) (mg/l).
5]Total solid (TS): (wt. of evaporating dish with sample residue after dryness – empty wt. of evaporating dish) x10^6 / Volume of sample taken. Unit = mg/L	4]Dissolved oxygen (DO) = (Total volume x 8 x Normality of sodium thiosulphate x1000)/ Volume of sample to be treated (mg/l)
6]Total suspended solids(T.S.S): = (TS – TDS) in mg/l.	5]Chemical oxygen demand(COD) = (Blank – Sample)x 8 x Normality of ferrous ammonium sulphate x 1000/ Volume of sample taken. (mg/l)

1.6 Detection of adulteration of bournvita/ horlicks/ milk powder present in sample: [7]

R&D of opium factory has developed its own method for detection of adulterants such as bournvita, horlicks or milk powder present in sample purchased from outside of the factory.

1.6.1 Milk powder and horlicks :

Its detection is based upon the principle that milk powder and horlicks contain casein as milk protein which gives color test with many coloring agents.

1.6.2 Bournivita:

Presence of cocoa butter and theobromine which is characteristic of bournvita, as these are components of cocoa or chocolate which can't be present in any other non-cocoa adulterant or the opium itself.

The second test distinguishing bournvita from milk powder and horlicks is casein test. The spot of casein is usually absent in the sample adulterated with bournvita.

- Finally sugar is not only present but is a major constituent of bournvita, horlicks and milk powder which will increase the sugar content of opium to high level thereby bringing the sugar content of this adulterated sample to the detectable level.In case of opium unadulterated with bournvita, horlicks or milk powder either no spot is developed or if a spot is developed it is light brown in color which may be easily distinguished from the grayish spot of adulterated materials.

1.6.3 Tests for detection of bournvita/ horlicks/ milk powder in a given sample using TLC:

- ***Vanillin test:***

Sample adulterated with bournvita, horlicks or milk powder gives black to grayish black spot with vanillin reagent on TLC plate. This test is specific for sugars such as lactose, fructose, glucose or sucrose.

Sugars give a black to grayish black color with vanillin reagent on TLC plate, since bournvita, horlicks or milk powder contain considerable amount of sugar a positive test of sugar is obtained when sample is adulterated with them even with 5% of these products.

4. Dimethyl amino benzaldehyde test:

It is developed for identification of horlicks or milk powder. Development of blue/indigo colored ring on periphery at the origin of spot indicates the presence of horlicks or milk powder.

Table 3: Different cases in detection of adulterants in sample using TLC

CASES	OBSERVATION	INFERENCES
CASE 1	i)blue/indigo colored ring on periphery at the origin of spot. ii)black to grayish black spot at 0.52 Rf.	Milk powder & horlicks is present in sample.
CASE 2	i) No blue/indigo colored ring on periphery at the origin of spot. ii)black to grayish black spot at 0.52 Rf.	Bournvita is present in sample.
CASE 3	i)No blue/indigo colored ring on periphery at the origin of spot. ii) No black to grayish black spot at 0.52 Rf.	No adulteration is present in the sample.

1.7 Results & Discussions:

Table 4: Analysis of water samples of ETP plant

(inlet & outlet water samples):

Parameters	Inlet water sample	Outlet water sample
COLOR	Brownish yellow	Pale yellow
ODOR	Pungent smell	Pungent smell
TEMPERATURE	29ºC	30ºC

Parameters	Inlet water sample	Outlet water sample
PH	8.94	8.25
TDS	400 mg/l	288 mg/l
TS	2200 mg/l	300 mg/l
TSS	1800 mg/l	12 mg/l
COD	300 mg/l	144 mg/l
TOTAL HARDNESS	178 mg/l	140 mg/l
CALCIUM HARDNESS	132 mg/l	136 mg/l
MAGNESIUM HARDNESS	46 mg/l	30mg/l

Table 5: Detection of adulteration in sample A:

S.NO	OBSERVATIONS	INFERENCE
1.	i)No blue/indigo colored ring on periphery at the origin of spot. ii) No black to grayish black spot at 0.52 Rf.	No adulteration is present in the sample A i.e sample A is pure.

Discussions

- In the form of tables the result of this experiment correlated with the ideal parameters of industrial waste water discharge.
- Since from the table of analysis of two different water samples of ETP i.e Inlet and Outlet waste water samples, it is clear that the data of outlet water sample of ETP is quietly obeying the standard data of effluent given by difference agencies like WHO, ISI etc. Thus we can say that outlet of ETP may not be fit for drinking but can be beneficial for gardening & minimization of river water pollution.
- From the table of adulteration detection in sample A, it is clear that sample A is pure and unadulterated with bournvita, horlicks or milk powder.

1.8 Future prospects

Today is the age of making things eco-friendly as nature & human being are inter-related and if we destroy our environment severely then one day it will lead to destruction of human beings too. So, we can say that every effluent releasing industries has to set up an ETP for treating the effluent and to make industries eco-friendly.As the R&D ofthis factory has developed their own method for detection of adulteration using a simple technique of TLC, research should be done to evolve likewise technique which should be cheap and simple to operate giving good results.

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