Chemical procedures to detect carcinogenic compound in domestic wastewater

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Abstract. This review presents chemical methods to detect carcinogenic compound in wastewater. Atomic absorption spectroscopy (AAS), high performance liquid chromatography (HPLC) and gas chromatography mass spectroscopy (GCMS) and their alternative attached equipments were discussed. The application of each method is elaborated using related studies in the field.

1. Introduction
Cancer is a leading cause of death worldwide. The death rates due to cancer are very common in the developing countries. It is estimated that the mortality rates could further increase to more than 13.1 million people per year by the year 2030 [1]. Carcinogen is a compound that has the potential to cause cancer to humans under certain concentrations or periods of exposure [2, 3]. The water-borne contaminants such as heavy metals ion, polycyclic aromatic hydrocarbons (PAHs), N-nitroso compounds, mycotoxins and Heterocyclic Amines (HCAs) are carcinogenic upon consumption [4-9]. Domestic wastewater is wastewater of residential areas origin. It is mainly from the substances of human metabolism and household activities. Over 90% of the carcinogenic loading comes from the domestic areas. These areas can achieve loading values greater than industrial zones with standard loading over discharging rate of more than 10^9 L/d. The strong correlation between cancer and the presence of pollutants in wastewater have been proclaimed in previous studies [10-13]. Therefore, standards supervision and accurate measurement of carcinogenic compounds in domestic wastewater is highly in demand. This review gives descriptions on the detection and measurement methods of carcinogens in domestic wastewaters via chemical approaches. Therefore, the selection on the most appropriate method of detection and measurement can be made. The evaluations are based on advantages and disadvantages, accuracy, speed and time factor of methods and experimental procedures.

2. Detection Methods
Extraction, purification and identification of organic contaminants analyses demands the use of high technology equipments such as atomic absorption spectrophotometer (AAS), high performance liquid chromatography (HPLC) and gas chromatography mass spectrometer (GCMS).

2.1 Atomic Absorption Spectroscopy (AAS)
Atomic Absorption Spectroscopy (AAS) is an analytical procedure to determine the types of metals or metalloids and their concentrations in environmental samples. It employs the absorption of optical
radiation of detected metal or metalloid at its gaseous phase. The heavy metals and metalloids contamination can be found in geothermal sources, volcanic and industrial effluents from mining, petrochemical industry, landfills resulting in pollution to the groundwater, soil and aquatic ecosystems. Analytical methods such as flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), electrothermal atomic absorption spectrometry (EAAS) and inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP MS) have been applied to direct determination of heavy metal. The GFAAS is the most sensitive technique.

Analysis of arsenic was carried out in West Bengal in India and Bangladesh. Atomic absorption spectrophotometry with vapour generation assembly (AAS VGA) technique was used for the detection method on arsenic. Total arsenic analysis \([\text{As(III)} + \text{As(V)}]\) requires reduction of As(V) to As(III). As(III) is reduced to AsH\(_3\) vapours and finally to free As atoms, which are responsible for absorption signal in AAS. The vapour generation assembly attached to AAS has acid channel filled with 10 M HCl and the reduction channel with sodium borohydride. The test conditions for the reduction of the sample in the instrument directly and introduction of KI in the reduction channel along with the sodium borohydride. It is observed that the acid concentration of the sample plays an important role. Further reduction in acid concentration and analysis time is achieved for the arsenic analysis using modified method. Analysis in both of the methods is sensitive at ppb level [14].

The levels of some heavy metals in groundwater, mixed water and wastewater in Alahsa farms, Saudi Arabia were examined. The total contents of Mn, Fe, Cu, Zn, Cd and Pb were determined using GFAAS. The level of heavy metals in groundwater and mixed water were found suitable for irrigation purpose based on the recommendation by the Food and Agriculture Organization. However, the spatial distribution study of Mn and Fe in groundwater in the area under this study was found to increase from southeast to northwest [15].

2.2 High Performance Liquid Chromatography (HPLC)

High performance liquid chromatography (HPLC) instruments consist of a reservoir mobile phase, a pump, an injector, a separation column and a detector. Compounds are separated by injecting a plug of the sample mixture onto the column. The different components in the mixture pass through the column at different rates due to differences in their partitioning behaviour between the mobile liquid phase and the stationary phase. HPLC is one of the most powerful tools in analytical chemistry. It has the ability to separate, identify and quantify the compounds in any sample that can be dissolved in a liquid. Compounds in trace concentrations as low as parts per trillion (ppt) may easily be identified.

HPLC with UV detector is a method used for detection of HCAs in wastewater. HPLC with fluorescence detection is used to detect PAHs and also used for the analysis of pyrolytic mutagen type heterocyclic amines [16]. HCAs have UV characteristics spectra and high extinction coefficients. Therefore, these compounds can be measured with UV detector. UV detector is the most preferable and HCAs can be simultaneously detected at 260-275 nm. HCAs such as Trp-P-1 and Trp-P-2 can be detected using this UV detector. The column chromatography like tSK gel ODS-120A column that used in HPLC provides the best peak symmetry and separation efficiency result [16-18].

Some researchers combined solid phase extraction with HPLC and UV detector and combined HPLC with fluorescence with Gas Chromatography (GC) and AAS. The HPLC with UV detector is a prominent method for analytes detection in research areas due to its frequent availability in the market and its capability of multi samples analysis concurrently with a high accuracy [17].

2.3 Gas Chromatography Mass Spectrometry (GCMS)

Gas chromatography mass spectrometry (GCMS) is a method that combines the features of gas liquid chromatography and mass spectrometry to identify different substances within a test sample. GC can separate volatile and semi-volatile compounds with great resolution but it cannot identify the components. MS can provide detailed structural information on most compounds but it cannot readily
separate them. GC and MS are highly compatible techniques which solve the above mentioned barriers.

A new methodology for the separation, identification and quantification of eight \( N \)-nitrosamines was developed using raw sewage and final-discharge wastewater. The method was based on solid phase extraction (SPE) and a purification technique followed by GC analysis equipped with a triple-quadrupole MS gave an effective separation of the targeted compounds. The limits of detection of this method for \( N \)-nitrosamines ranged from 0.1 to 1.0 ngL\(^{-1}\) and the limits of quantification ranged from 0.4 to 3.3 ngL\(^{-1}\) [19].

A multiclass screening method for organic contaminants in surface water, groundwater and effluent wastewater was developed by Portolet et al. [20]. The screening is based in the use of GCMS/ToF, and the sample procedure involved solid phase extraction with C\(_{18}\) cartridges. Around 150 organic contaminants from different chemical families were investigated, including PAHs, octyl/nonyl phenols, PCBs, PBDEs and a notable number of pesticides and several relevant metabolites. Surface water, ground water and effluent wastewater were found contained all target analytes at three concentration levels (0.02, 0.1 and 1 \( \mu \text{g} \text{L}^{-1} \)). Influent wastewater and raw leachate from a municipal solid waste treatment plant were spiked at two levels (0.1 and 1 \( \mu \text{g} \text{L}^{-1} \)). The identification of compounds in influent wastewater was more problematic at concentration of 0.1 \( \mu \text{g} \text{L}^{-1} \). Overall, many contaminants could be properly identified at the lowest level 0.02 \( \mu \text{g} \text{L}^{-1} \) in cleaner matrices. The procedure was applied to the screening of water samples of different origin and matrix composition and allowed the detection of several target contaminants [20].

3. Conclusion

Carcinogenic compounds are a group of chemicals that can cause chromosomal aberrations, resulting in cancer. The presence of carcinogens has been reported in domestic wastewater. Sewage treatment plants inefficient performance cause release of these hazardous compounds to surrounding watercourses. Chemical methods are precise and fast approach to detect the carcinogens presents in the water and wastewater. Carcinogens can be identified accurately using an appropriate method chosen from the available alternatives. Although chemical methods such as AAS, HPLC and GCMS are recommended as detection tools, the possession, operations and maintenances cost of these methods is the main drawback for their wide application.

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