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Synchrotron Based TXRF for Assessment of Treated Wastewater

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ABSTRACT

The use of wastewater for diverse applications is gaining popularity for protecting scarce freshwater resources. The global supply of freshwater is limited and is threatened by the masses. Communities are competing over the allocation of limited freshwater resources to meet the increasing demand for water for agriculture, industry and cities. Wastewater treatment units are being used to treat wastewater for irrigation, firefighting, and other domestic purposes. The environment and human health can be adversely affected if wastewater is not accurately treated. Treated wastewater if free from toxicity can help in preserving the natural environment. In the present work, the synchrotron-based Total Reflection X-ray Fluorescence (TXRF) has been used to assess the trace elements present in the treated wastewater collected from a sewerage treatment plant in the study area. The results are compared with the World Health Organization (WHO) recommended values and concluded that the concentration of all detected elements (Cr, Mn, Ni, Cu, Zn and Pb) are within permissible limits (except iron). Investigations are further incorporated in calculations of the water quality index (WQI) that is used for the treated water standards. The present WQI 82.70 lies in the good quality range 80-94 by Canadian Council of Ministers of the Environment (CCME 2001) standards and does not pose any hazard to the environment, therefore, recommended for irrigation, toilet flushing, firefighting etc.

INTRODUCTION

Approach to freshwater is crucial for anthropological development, the environment and the economy. More than two billion people have a paucity to clean drinking water and hygiene (World Health Organization 2017) that blocks continual growth attempts worldwide. The increasing burden on existing water resources has resulted in higher water paucity and an expanding need for adequate quality water. An integrated *One Water* concept can facilitate meeting this demand by limiting discharges from wastewater treatment (Mitchell 2006). Three general types of water reuse include agricultural, environmental, and industrial applications. The main objective of wastewater treatment is to abolish as much of the pollutants as possible before the remaining water, called effluent, can be discharged back to the environment. Water reuse produces substantial environmental benefits. It helps in mitigating the adverse effects of sewage or industrial effluent on the environment. The end use of wastewater decides the required water quality and management measures to ensure safety. World health organization and other countries have provided guidelines and standards for the secure use of wastewater in irrigation and other environments (WHO 2006).

Water sample analysis in terms of trace elements and their concentration is a topic of great concern in many fields. It can be done by a number of procedures. Researchers have used various methods like atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and X-ray fluorescence (XRF) technique to analyse the elemental quantification of water samples. Bamford et al (2004) applied XRF technique for trace elemental analysis of environmental samples e. g. soil, water and plants and recommended XRF for determination of elements in the range Na to U. Melquiades et al. (2004) used XRF technique for simultaneous heavy metal contamination in water. X-ray fluorescence is considered as a non-destructive simultaneous analysis of the sample, but the use is preferred for solid samples only (Margui 2014). TXRF (total reflection X-ray fluorescence) is another version of X-ray fluorescence technique, where the intricacy of the Compton spectral background is eradicated to a large extent. This is due to the high reflectivity of the flat surface and low penetration depth of the primary X-ray beam in the substrate material, on which the incident X-rays can impinge at glancing incidence angles. The above characteristics enhance the detection sensitivities of TXRF technique by two or three times or higher compared to normal X-ray fluorescence: typically, in the range of parts per billion (ppb) (Tiwari 2018). Synchrotron radiation has multiple edges over conventional X-ray sources like monochromacy, high incident flux, high convergence, and linear polarization, which results in increased signal strength and reduced scattered background. Moreover, tunability of the incident photons energy to the characteristic absorption edge of an element identified in the sample leads to higher fluorescence intensities and hence making this technique appropriate for swift elemental analysis. TXRF is thus suitable for quickly studying all considered elements. TXRF spectroscopy has attracted interest in recent years. Examining the extraordinary competencies of synchrotron radiation, TXRF can be efficiently applied to detect trace concentrations of contaminants.

Water quality has been studied extensively in acceptable and standard ways by applying the water quality index (Tyagi et al. 2013). The possibilities of using treated wastewater for diverse applications need to be strengthened with elements of affordability, sustainability and above all public acceptance. In the present work, synchrotron-based TXRF has been used to measure the trace elemental concentration of treated wastewater collected from a sewerage treatment plant in the study area.

MATERIALS AND METHODS

To achieve a thin and homogenous sample layer 100 μL of polyvinyl alcohol was added to 10 mL of the treated water sample. 10 μL of gallium was added as an internal standard in the water sample. After complete homogenization, 10 μL of the liquid sample was placed on a siliconized quartz glass substrate and the sample was vacuum dried for about 10 minutes. The sample reflector carrying the water sample was placed in the experimental set-up as shown in Fig. 1 (a) and 1(b) along with other instrumentations involved in TXRF.

The measurements were performed on a synchrotron beam line 16 (BL-16) specially commissioned for X-ray fluorescence studies at Raja Ramanna Centre for Advanced Technology, Indore-India. The experimental arrangement of beam line (BL-16) consists of a double crystal monochromator with Si(111) symmetric and asymmetric crystals. The set-up also has focusing optics and a combination of slits to reduce the scattered X-ray background and improve the collimation of the X-ray beam. For accurate detection of trace elements present in the sample, the set-up is equipped with a silicon drift detector having an energy resolution of 129 eV at 5. 9 keV. The fluorescent spectra were recorded for 500 seconds. Fig. 1(a) depicts a schematic design of the TXRF set up at BL-16, whereas Fig. 1(b) shows an actual photograph of the TXRF set up at BL-16.

RESULTS AND DISCUSSION

Fig. 2 shows typical TXRF spectra obtained for sewerage treated water mixed with 10 ppm of Ga standard at 18 keV synchronous X-ray energy, whereas the inset shows fitted TXRF spectra of the same sample on a logarithmic scale. Solid black and red lines, respectively, are the experimental and fitted data, whereas the green line represents a good estimation of the spectral background.

Most of the trace elements Cr, Mn, Fe, Ni, Cu, Zn and Pb were identified in the treated water sample with the best detection sensitivity. The measured concentration of trace elements (ppb) in the treated water sample is listed in Table 1 and Fig. 3 along with the permissible WHO limits (2008). The comparison shows that the measured concentration of trace metals is within permissible standards for almost all the elements except iron that is more than 20 times of its permissible limit. The probabilistic reasons for the high content of iron may be geological deposits (regional soils, rocks), acidic nature of wastewater and chemical reactions enhancing iron concentration in the STP (EPA 2001). Many studies have also found that the presence of iron in huge amounts in the water can act as an adsorbent for the pollutants after making complexes in presence of some favourable chemical agents

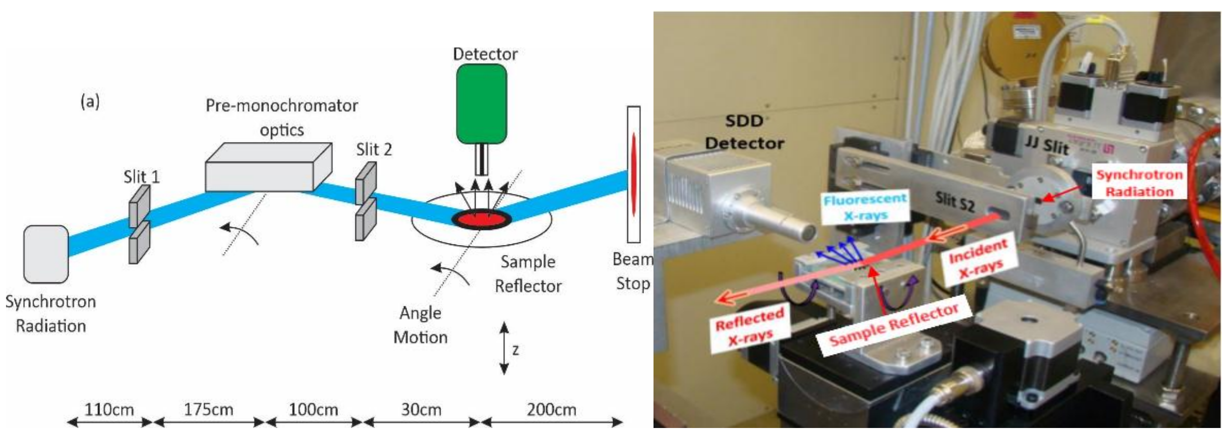

Fig. 1: (a) Schematic diagram of the experimental TXRF set-up developed at RRCAT (b) Actual photograph of the TXRF spectrometer.

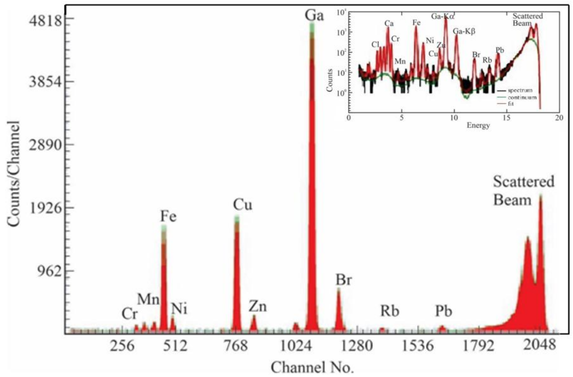

Fig. 2: Typical TXRF spectra obtained for sewerage treated water mixed with 10 ppm Ga standard at 18 keV. The inset shows fitted TXRF spectra of the same sample on a logarithmic scale.

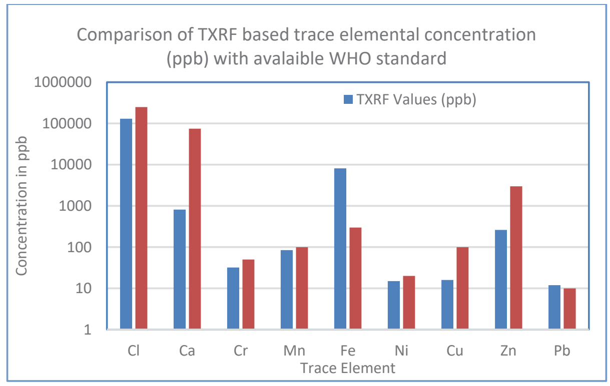

Fig. 3: Graphical representation of trace elemental concentration (ppb) in sewerage treated water mixed with 10 ppm Ga standard.

(Najafpoor et al. 2020). For example, nanoparticles of iron oxide are sufficient to remove (Hu et al. 2005) chromium, selenium, copper, lead, and nickel, from the simulated as well as natural waters (Zhang et al. 2016). It is also possible that the abundant iron present in water may get mixed with sludge and form complexes, which can act as an adsorbent for the removal of heavy metals from the water. Furthermore, both manganese, and nickel in treated water are observed as 85 ppb and 15 ppb, which are within quite safe levels as suggested by WHO (2006). Manganese is one of the most abundant metals in Earth's crust, usually occurring with Iron. Manganese, Iron and Nickel occur naturally in many food sources, leafy vegetables, nuts, grains, and animal products etc. Therefore, anthropological activities can also be responsible for the marginal concentration of Manganese and Nickel as compared to other trace elements in the treated water samples collected from domestic sewerage plant.

Water Quality Index (WQI)

The water quality index (WQI) is an essential mean to ascertain the water quality in urban, rural and industrial areas. WQI is documented by Canadian Council of Ministers

Table 1: The concentration of trace elements (ppb) in sewerage treated water along with WHO standards.

Sr No.	Trace metal (parameters)	TXRF results (7% uncertainty)	Permissible limits (WHO year)
1	Cl	130276(±9119.32)	250000
2	Ca	815(±57.05)	75000
3	Cr	32(±2.24)	50
4	Mn	85(±5.95)	100
5	Fe	8136(±569.52)	300
6	Ni	15(±1.05)	20
7	Cu	16(±1.12)	100
8	Zn	262(±18.34)	3000
9	Pb	12(±0.84)	10

of the Environment (CCME 2001). The index enables us to understand how far the physical parameters related to water quality surpass their respective limits. Therefore, WQI demonstrates water quality standards for all settings as determined by the World Health Organisation. WQI calculations are related to various physical, chemical, and bacteriological parameters, but in developing and underdeveloped nations, the primary concern is to provide affordable solutions due to limited funds (Ongley 1998, Ongley & Booty 1999). Therefore, in these type of circumstances, only major parameters can be used to calculate WQI (Kannel et al. 2007). The general WQI equation involves three factors as below (eq. i):

$$\mathrm{WQI} = 100 - \left(\frac{\sqrt{F_1^2+F_2^2+F_3^2}}{1.732}\right) \quad \ldots(1)$$

F1 represents the percentage of parameters that exceed the guideline, F2 represents the frequency with which the parameters exceed the guideline and F3 represents the magnitude by which the parameters have not met/exceeded. The individual values of parameters F1, F2 and F3 are calculated as follows.

$$\mathrm{F1} = \left(\frac{\text{Number of exceeded/unmet parameters}}{\text{Total number of parameters}}\,\mathrm{x}\right) 100 \quad \ldots(2)$$

$$\mathrm{F2} = \left(\frac{\text{Number of failed tests}}{\text{Total number of tests}}\,\mathrm{x}\right) 100 \quad \ldots(3)$$

$$\mathrm{F3} = \left(\frac{\text{Failed test value}}{\text{guideline Value}}\right) - 1 \quad \ldots(4)$$

The value of the factors F1, F2 and F3 calculated using equations (ii), (iii) and (iv) are 7.69, 12.5 and 26.12 respectively are substituted in equation (i) to produce WQI value (between 0 and 100) that characterizes water quality. WQI ranges and descriptions are:

Excellent (95-100)
Good (80-94)
Fair (65-79)

Table 2: Physical parameters like pH value, turbidity, total hardness and TDS of the water samples of study area along with reference ranges [*].

Sr. No.	Parameter	Jan, 2019	Feb, 2019	March, 2019	April, 2019	May, 2019	June, 2019	July, 2019	August, 2019	Reference range [*]
1	pH value	7.65	7.5	7.6	7.45	7.5	7.46	7.65	7.5	6.5-8.5
2	Turbidity (NTU)	4.5	4.5	4.5	5	4.5	4.5	5	5	1-5
3	Total hardness (mg/L)	180	190	180	184	185	180	184	185	200
4	TDS (mg/L)	85	80	80	85	85	80	90	85	500

*(Bureau of Indian Standards 2012)

Marginal (45-64) Poor (0-44)

In the present analysis, physical parameters like pH value, turbidity, total hardness, and TDS of the same water (Table 2) have also been taken into consideration for WQI calculations.

The water quality index (WQI) for the treated water is calculated by drawing analysis from Table 1 and Table 2 and the approximated value of the same is 82.70, which is considered as good quality as per CCME (2001).

CONCLUSION

The results of wastewater analysis show how synchrotron-based TXRF measurements can successfully be applied for multi-elemental analysis of liquid samples to simultaneously quantify almost all elements after a precise and systematic sample preparation technique. The detection sensitivities of the TXRF technique is far better compared to conventional XRF and other analytical methods. Synchrotron TXRF (SR-TXRF) is advantageous in terms of experimental time, minimum background, high monochromatic radiation flux along with sample preparation and calibration. It is concluded that the measured elemental concentration for almost all trace metals in the treated water is within permissible WHO guidelines (except iron). Furthermore, it is quite evident from the calculated value of the water quality index (WQI) that the treated water has no significant threats and can be recommended as an alternative to freshwater for irrigation, toilet flushing, firefighting etc in the study area.

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