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# Fertilizer industrial effluents: Physico-chemical characterization and water quality parameters evaluation



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#### ABSTRACT

In this study, effluents from four different fertilizer industrial units, producing different fertilizers have been analyzed for various physicochemical features. The color, odour, temperature, pH, electrical conductivity (EC), total dissolved solids (TDS), Biochemical oxygen demand (BOD), chemical oxygen demand (COD), chloride (Cl<sup>-</sup>), fluoride (F<sup>-</sup>), carbonate ( $CO_3^2^-$ ), bicarbonate ( $HCO_3^1^-$ ), ammonia (NH<sub>3</sub>), nitrate ( $NO_3^-$ ), nitrite ( $NO_2^-$ ), phosphate ( $PO_4^{4-}$ ), sulphate ( $SO_4^{2-}$ ), solium (Na), potassium (K), calcium (Ca), magnesium (Mg), zinc (Zn), chromium (Cr) and lead (Pb) were determined using standard analytical procedures. The values of measured parameters were found significantly (P < 0.05) higher than the permissible limits recommended for wastewater. In comparison to national environmental quality standards, it was concluded that the effluents from fertilizer industries require proper treatment prior to discharge into the environment.

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#### 1. Introduction

The importance of fertilizer industry in an agricultural country like Pakistan is vital; as 70% of the population is linked with agricultural means of employment [1]. During 1952–53, marketing of high yielding cereal crops, having high nutrient requirements, reformed fertilizer industry, resulted in production and commercialization of various fertilizer products in Pakistan (1966–67) and there have been a continuous rise in their demand. Annual production of fertilizers recorded in 2000–01 was 851% higher than in 1969–70, which indicates tremendous rise in demands of fertilizer in Pakistan [2].

Industrial units producing various fertilizer products are surely considered as backbone of agriculture. On the contrary, such industries are also among the major contributors of environmental pollution by means of gaseous, liquid and solid wastes emission. Fertilizer, pharmaceutical, tanning and dying related industries are continuously discharging their effluents containing toxic anions, organic and inorganic compounds, dissolved gasses pesticides and heavy metals as the major pollutants [3–32]. Therefore, regular and reliable characterization of liquid effluents is required for the proper treatment before disposal [11–13,15–22,24–27,31–34]. In many recent studies, textile mill [35],

\* Corresponding author. E-mail address: Bosalvee@yahoo.com (M. Iqbal). TNT industry [36], refinery [37], and olive mill wastewater [38] have been characterized and water quality parameters were found to be beyond the permissible limits. Similarly, this research work is aimed to characterize the effluent from different fertilizer units to evaluate their physicochemical features. For the purpose, effluent samples were collected from four industrial units, two (U-1 & U-2) of them were producing urea, third (AS) was the production unit of diammonium sulphate and fourth (NP) was Nitrophos and Calcium Ammonium Nitrate industry. Furthermore, results regarding physicochemical features of effluent were compared with standards furnished by National Environmental Quality Standard [9] to assess pollution potential of these effluents.

#### 2. Materials and methods

#### 2.1. Glassware and reagents

All the volumetric glassware was "A" grade calibrated. pH meter (Jenway 3505, UK) was used for pH measurement of all the samples, whereas EC and TDS were determined using electrical conductivity meter (Inolab, Germany). Spectrophotometer (Sanyo SP-50) was used for the determination of Nitrate, Sulphate, Phosphate, and Chromium ions in the effluents.

All the reagents were of Reagent grade. Double distilled water and deionized water were used throughout the studies.

#### 2.2. Sampling procedures

Four industrial units, producing different fertilizers were chosen for collection of effluent samples i.e. two samples (U-1 & U-2) were collected from two different industrial units producing Urea, sample (AS) from unit producing diammonium sulphate and one (NP) from the unit producing Nitrophos and Calcium ammonium nitrate as a product. Glass and polyethylene bottles were used for the preservation of samples. Chemical stabilization was performed in different bottles as required. Mercuric chloride was added for the preservation of samples to analyze different forms of nitrogen and phosphorous. Nitric acid and sulfuric acid were used as preservatives for the determination of metals and COD in different bottles, respectively.

#### 2.3. Physicochemical analysis of effluents

Standard methods were used for the analysis of wastewater. Color, odour, temperature, pH, EC, and TDS were determined at the spot. While the other determinations were done in the laboratory as;

Spectrophotometric and titrimetric methods of analyses were used for the analysis of wastewater. Ammonia was determined using Nessler reagent, sulphate using gum acacia, nitrate using brucine reagent, and phosphate using ammonium molybdate as a reagent spectrophotometrically [39,40]. Chemical oxygen demand was estimated by titration proceeded by oxidation using potassium dichromate as an oxidizing agent, BOD<sub>5</sub> test was performed by iodometric titrations, carbonate and bicarbonates by acid base titration, Chlorides by argentometric titration fluorides by SPADNS method using colorimeter and nitrites were estimated by redox titration [39–41].

The metal contents like Na, K, Ca, Mg, Zn, Cr and Pb were determined using atomic absorption spectrometer (Shimadzu AA 6300) having Air-Acetylene flame with 2300 °C temperature. Standard curves were made using commercial standards after proper dilutions.

#### 3. Results and discussion

The collected effluent was evaluated in terms of color, odour, temperature, pH, electrical conductivity (EC) and total dissolved salts (TDS) and results are summarized in Table 1. The color of all the samples was slightly blackish, while odour was observed ammoniacal with slight difference among the samples. The values of temperature and pH were recorded 41 °C and 9.9 for AS and NP effluents, respectively. High pH of wastewater may enhance the solubility of many essential elements like Se, instead of other elements like Al, B, Cd, Fe, Mn, and Hg and if released in canals, streams and river then it may affect aquatic life as it possesses potential to alter the toxicity and solubility of pollutants. The evaluation of EC and TDS indicates the presence of salts in the samples. Among the investigated effluent samples, high EC and TDS values were recorded for NP and AS samples; indicating their ability to increase salinity of water bodies that may cause adverse ecological effects on aquatic biota [42].

Chemical characterization of wastewater was done by estimating biochemical oxygen demand (BOD), chemical oxygen demand (COD), nutrients and heavy metals [43]. High BOD and COD of effluent samples indicate the presence of high concentration of organic and inorganic matter. The maximum recommended values of BOD and COD in NEQS are 200 and 400 mg/L, respectively. Fig. 1 indicates that for all the

#### Table 1

Color, odor, temperature, pH, electrical conductivity of different fertilizer industries wastewater.

	Color	Odor	Temperature °C	рН	EC S/m	TDS mg/L
U-1	Nill	Ammoniacal	35	9.2	3457	1593
U-2	Nill	Nill	39	9.5	2861	1357
AS	Dirty	Bitter	41	9.0	5942	3648
NP	Brownish	Bitter	38	9.9	8608	2254



Fig. 1. Chemical oxygen demand, biochemical oxygen demand, carbonates, bicarbonates and chloride (mg/L) contents of fertilizer industries wastewater.

samples, both the oxygen demands are higher than NEQS recommended values. Effluent samples from industry producing Nitrophos and Diammonium Phosphate (NP) were found to have maximum value, indicating the potential of sample NP to promote algal blooms and destabilize aquatic systems and reason may be the presence of high amounts of nutrients [42].

Carbonates and bicarbonates in tested effluent samples were high but concentration of chlorides was less than the limit prescribed in NEQS. High content of carbonates and bicarbonates may alter pH as well as alkalinity of water, while chlorides may not have any hazardous impact on the environment. However, small amount of chlorides may be helpful during treatment process i.e. removal of organic matter, nitrogen and phosphorous from wastewater [44].

The amount of nutrients including nitrate, nitrite, ammonia, sulphate and phosphate estimated in effluents from different fertilizer industries is presented in Fig. 2. Among the tested samples, NP possesses high amounts of all the nutrients except sulphate and phosphate. These concentrations were even greater than the values prescribed in national environmental quality standards (NEQS). High amount of nitrates and nitrites may be due to the products of NP industry contain nitrates as its constituent. Reports reveal that compounds containing heavy amounts of nitrogen in water bodies may lead towards formation of carcinogenic compounds like nitrosamines and nitrosamides, which are harmful for living organisms [45]. If they become the part of drinking water, then nitrite may enter in blood stream that can disturb oxygen transporting substance (hemoglobin) to methemoglobin, which neither carry oxygen and is nor converted to hemoglobin again, this condition is called methemoglobinemia. Furthermore, it can also interfere with other iron containing proteins and all these conditions may result in fetal death from hypoxia [46].

The AS sample contains higher amount of sulphates, even greater than the permissible limits given in NEQS (600 mg/L). The presence of high amounts of phosphorus and nitrogen in wastewater may cause eutrophication of aquatic systems, which results in deficiency of oxygen in



Fig. 2. Nutrients (mg/L) content of fertilizer industries wastewater.

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