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

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Umer Younas [a,b], Shahid Iqbal [a], Asif Saleem [c], Munawar Iqbal [b,*], Arif Nazir [b], Sajida Noureen [d], Karamat Mehmood [d], Numrah Nisar [e]

[a] Department of chemistry, University of Sargodha, Sargodha 40100, Pakistan
[b] Department of Chemistry, The University of Lahore, Lahore 54000, Pakistan
[c] Institute of Molecular Biology and Biotechnology (IMBB), The University of Lahore, Lahore 54000, Pakistan
[d] Department of Chemistry, The Islamia University of Bahawalpur, Pakistan
[e] Department of Environmental Sciences, Lahore College for Women University Lahore, Lahore, Pakistan.

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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^-), fluoride (F^-), carbonate (CO_3^{2-}), bicarbonate (HCO_3^{1-}), ammonia (NH_3), nitrate (NO_3^-), nitrite (NO_2^-), phosphate (PO_4^{3-}), sulphate (SO_4^{2-}), sodium (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],

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.

* Corresponding author.
E-mail address: Bosalvee@yahoo.com (M. Iqbal).

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_5 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
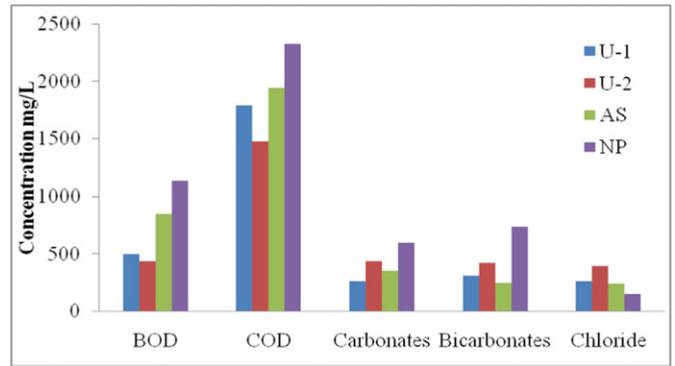
Table 1
Color, odor, temperature, pH, electrical conductivity of different fertilizer industries wastewater.

	Color	Odor	Temperature °C	pH	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
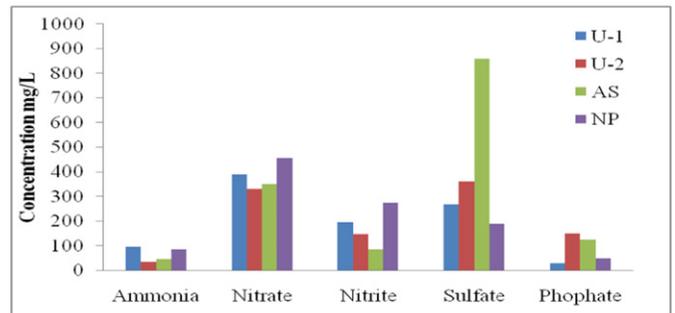

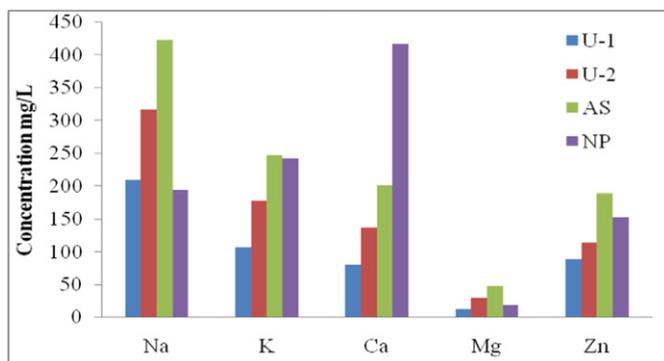**Fig. 2.** Nutrients (mg/L) content of fertilizer industries wastewater.

Fig. 3. Metal ions (mg/L) contents of fertilizer industries wastewater.

the water and is dangerous for aquatic life [47]. Effluent samples from industrial unit U-2 were found to be containing high amounts of phosphate that may have negative effect on environment, where wastewater is being discharged by the industry.

The amounts of Na, K, Ca, Mg and Zn are presented in Fig. 3. The AS sample contains high amount of all the metals except calcium, which was found in excess in NP sample. These results demonstrate that effluents from fertilizer industry are potent for altering the chemistry of subsurface as well as canal water.

Fig. 4 presents concentration of chromium (Cr), fluoride (F) and lead (Pb) in different effluent samples. The amount of fluoride and Pb was tremendously high in NP, which reveals its potential to pollute the environment. Lead is one of the toxic heavy metals that may damage liver and kidneys. Although, fluoride plays an imperative role in reducing dental caries, but ingestion of high amount of fluorides may cause enamel and skeletal fluorosis as well as bone fracture [9]. Chromium was also estimated in all the effluent samples and its concentration was found higher in U-1 among the tested samples as well as NEQS standard value (1 mg/L). Hexavalent form of chromium is the most toxic form as it possesses ability to cross the cell membrane and to make complex with genetic material after getting reduced to trivalent form, which is responsible for the toxic and mutagenic activities [48]. Therefore, effluent from industrial unit producing urea (U-1) can be considered as unfit for discharge in environment.

4. Conclusions

The physicochemical characterization of effluents collected from different fertilizer industries was performed and responses were compared with National Environmental Quality Standards (NEQS). The pH, EC, TDS, BOD, COD, Cl^-, F^-, CO_3^{2-}, HCO_3^{1-}, NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}, metal ions (Na, K, Ca, Mg, Zn, Cr and Pb) values were found to be beyond the permissible limits recommend for wastewater. Results indicates that the fertilizer industries effluents need emphasize of environmental protection agency of Pakistan and there is also a need to develop simple
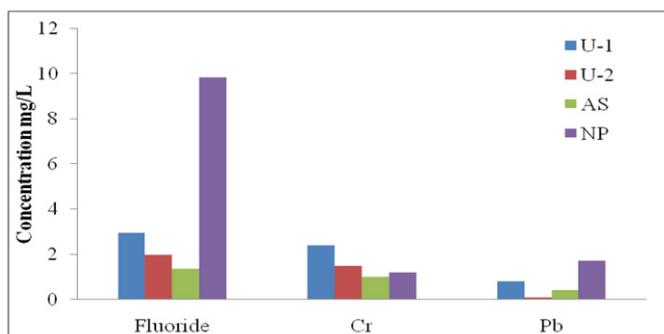

Fig. 4. Fluoride, chromium and lead (mg/L) contents of fertilizer industries wastewater.

and efficient treatment technologies for the remediation of wastewater to avoid environmental pollution for sustainable environmental development.

References

[1] A.K. Tripathi, S.N. Pandey, Water Pollution, APH Publishing, New Delhi, 1990.
[2] M.A. Quddus, M.W. Siddiqi, M.M. Riaz, The demand for nitrogen, phosphorus and potash fertilizer nutrients in Pakistan, Pak. Econom. Soc. Rev. 101-16 (2008).
[3] C. Namasivayam, D. Sangeetha, R. Gunasekaran, Removal of anions, heavy metals, organics and dyes from water by adsorption onto a new activated carbon from Jatropha husk, an agro-industrial solid waste, Process Saf. Environ. Prot. 85 (2007) 181–184.
[4] V. Garg, P. Kaushik, Influence of short-term irrigation of textile mill wastewater on the growth of chickpea cultivars, Chem. Ecol. 22 (2006) 193–200.
[5] B. Hammadi, A.A. Bebba, N. Gherraf, Degradation of organic pollution aerated lagoons. In an arid climate: the case the treatment plant Ouargla (Algeria), Acta Ecol. Sin. 36 (2016) 275–279.
[6] Z. Juan, C. Bin, Y. Wei-Wei, H. Hao, Study on coastal wetland habitat quality evaluation in Quanzhou Bay, Fujian, China Acta Ecol. Sinica 31 (2011) 264–270.
[7] M.S. Podder, C.B. Majumder, Arsenic toxicity to *Chlorella pyrenoidosa* and its phycoremediation, Acta Ecol. Sin. 36 (2016) 256–268.
[8] Z. Xie, J. Zhang, K. Cai, Z. Xu, D. Wu, B. Wang, Temporal and spatial distribution of macrobenthos communities and their responses to environmental factors in Lake Taihu, Acta Ecol. Sin. 36 (2016) 16–22.
[9] M.A. Zahed, F. Rouhani, S. Mohajeri, F. Bateni, L. Mohajeri, An overview of Iranian mangrove ecosystems, northern part of the Persian Gulf and Oman Sea, Acta Ecol. Sin. 30 (2010) 240–244.
[10] S. Amadi, C. Ukpaka, Role of molecular diffusion in the recovery of water flood residual oil, Chem. Int. 2 (2015) 103–114.
[11] A. Babarinde, K. Ogundipe, K.T. Sangosanya, B.D. Akintola, A.O. Elizabeth Hassan, Comparative study on the biosorption of Pb(II), Cd(II) and Zn(II) using Lemon grass (*Cymbopogon citratus*): kinetics, isotherms and thermodynamics, Chem. Int. 2 (2016) 89–102.
[12] A. Babarinde, G.O. Onyiaocha, Equilibrium sorption of divalent metal ions onto groundnut (*Arachis hypogaea*) shell: kinetics, isotherm and thermodynamics, Chem. Int. 2 (2016) 37–46.
[13] N.K. Benabdallah, D. Harrache, A. Mir, M. de la Guardia, F.Z. Benhachem, Bioaccumulation of trace metals by red alga *Corallina elongata* in the coast of Beni Saf, west coast Algeria, Chem. Int. 3 (2017) 220–231.
[14] A.M. Engida, B.S. Chandravanshi, Assessment of heavy metals in tobacco of cigarettes commonly sold in Ethiopia, Chem. Int. 3 (2017) 213–219.
[15] M. Iqbal, R.A. Khera, Adsorption of copper and lead in single and binary metal system onto *Fumaria indica* biomass, Chem. Int. 1 (2015) 157b–163b.
[16] S. Jafarinejad, Control and treatment of sulfur compounds specially sulfur oxides (SOx) emissions from the petroleum industry: a review, Chem. Int. 2 (2016) 242–253.
[17] S. Jafarinejad, Recent developments in the application of sequencing batch reactor (SBR) technology for the petroleum industry wastewater treatment, Chem. Int. 3 (3) (2017) 241–250.
[18] M.A. Jamal, M. Muneer, M. Iqbal, Photo-degradation of monoazo dye blue 13 using advanced oxidation process, Chem. Int. 1 (2015) 12–16.
[19] K. Legrouri, E. Khouya, H. Hannache, M. El Hartti, M. Ezzine, R. Naslain, Activated carbon from molasses efficiency for Cr(VI), Pb(II) and Cu(II) adsorption: a mechanistic study, Chem. Int. 3 (2017) 301–310.
[20] A.O. Majolagbe, A.A. Adeyi, O. Osibanjo, Vulnerability assessment of groundwater pollution in the vicinity of an active dumpsite (Olusosun), Lagos, Nigeria, Chem. Int. 2 (2016) 232–241.
[21] A.O. Majolagbe, A.A. Adeyi, O. Osibanjo, A.O. Adams, O.O. Ojuri, Pollution vulnerability and health risk assessment of groundwater around an engineering landfill in Lagos, Nigeria, Chem. Int. 3 (2017) 58–68.
[22] K.D. Ogundipe, A. Babarinde, Comparative study on batch equilibrium biosorption of Cd(II), Pb(II) and Zn(II) using plantain (*Musa paradisiaca*) flower: kinetics, isotherm, and thermodynamics, Chem. Int. 3 (2017) 135–149.
[23] R. Patel, S. Kumar, A. Verma, S. Srivastava, Kinetic and thermodynamic properties of pharmaceutical drug (Gabapentin) by potassium bromate (KBrO₃) in presence of micro amount of Ir(III) chloride as catalyst in acidic medium, Chem. Int. 3 (2017) 158–164.
[24] K. Qureshi, M. Ahmad, I. Bhatti, M. Iqbal, A. Khan, Cytotoxicity reduction of wastewater treated by advanced oxidation process, Chem. Int. 1 (2015) 53–59.
[25] A. Shindy, Problems and solutions in colors, dyes and pigments chemistry: a review, Chem. Int. 3 (2017) 97–105.
[26] H. Shindy, Basics in colors, dyes and pigments chemistry: a review, Chem. Int. 2 (2016) 29–36.
[27] C. Ukpaka, Development of model for bioremediation of crude oil using *Moringa* extract, Chem. Int. 2 (2016) 19–28.
[28] C. Ukpaka, Predictive model on the effect of restrictor on transfer function parameters on pneumatic control system, Chem. Int. 2 (2016) 128–135.
[29] C. Ukpaka, Empirical model approach for the evaluation of pH and conductivity on pollutant diffusion in soil environment, Chem. Int. 2 (2016) 267–278.
[30] C. Ukpaka, BTX degradation: the concept of microbial integration, Chem. Int. 3 (2016) 8–18.
[31] C. Ukpaka, T. Izonowei, Model prediction on the reliability of fixed bed reactor for ammonia production, Chem. Int. 3 (2017) 46–57.

[32] C.P. Ukpaka, F.U. Igwe, Modeling of the velocity profile of a bioreactor: the concept of biochemical process, Chem. Int. 3 (2017) 258–267.

[33] U.C. Peter, U. Chinedu, Model prediction for constant area, variable pressure drop in orifice plate characteristics in flow system, Chem. Int. 2 (2016) 80–88.

[34] M. Sayed, Efficient removal of phenol from aqueous solution by the pulsed high-voltage discharge process in the presence of H_2O_2, Chem. Int. 1 (2015) 81–86.

[35] A.Z. Gotvajn, J. Zagorc-Koncan, Characterization of textile wastewater: its environmental impact and biotreatability, Chem. Biochem. Eng. Q. 18 (2004) 309–315.

[36] M. Barreto-Rodrigues, F.T. Silva, T.C.B. Paiva, Characterization of wastewater from the Brazilian TNT industry, J. Hazard. Mater. 164 (2009) 385–388.

[37] M. Al Zarooni, W. Elshorbagy, Characterization and assessment of Al Ruwais refinery wastewater, J. Hazard. Mater. 136 (2006) 398–405.

[38] E.S. Aktas, S. Imre, L. Ersoy, Characterization and lime treatment of olive mill wastewater, Water Res. 35 (2001) 2336–2340.

[39] K. Helrich (Ed.), Official Methods of Analysis, 15th Edition, The Association of Official Analytical Chemists, Inc., Arlington, 1990.

[40] Q.H. Jaffery, J.B. Asisett, Vogel's Textbook of Quantitative Inorganic Chemical Analysis, fifth ed. John Wiley and Sons, 1989.

[41] F.W. Fifield, P.J. Haines, Environmental Analytical Chemistry, Wiley-Blackwell, 2000.

[42] J. Akan, F. Abdulrahman, G. Dimari, V. Ogugbuaja, Physicochemical determination of pollutants in wastewater and vegetable samples along the Jakara wastewater channel in Kano Metropolis, Kano State, Nigeria, Eur. J. Sci. Res. 23 (2008) 122–133.

[43] V. Garg, P. Kaushik, Influence of textile mill wastewater irrigation on the growth of *Sorghum cultivars*, Appl. Ecol. Environ. Res. 6 (2008) 1–12.

[44] C.C. Hong, S.K. Chan, H. Shim, Effect of chloride on biological nutrient removal from wastewater, J. Appl. Sci. Environ. Sanitat. 2 (2007) 85–92.

[45] Y. Fernandez-Nava, E. Maranon, J. Soons, L. Castrillon, Denitrification of wastewater containing high nitrate and calcium concentrations, Bioresour. Technol. 99 (17) (2008) 7976–7981.

[46] A.M. Fan, C.C. Willhite, S.A. Book, Evaluation of the nitrate drinking water standard with reference to infant methemoglobinemia and potential reproductive toxicity, Regul. Toxicol. Pharmacol. 7 (1987) 135–148.

[47] K. Davidson, R.J. Gowen, P. Tett, E. Bresnan, P.J. Harrison, A. McKinney, S. Milligan, D.K. Mills, J. Silke, A.M. Crooks, Harmful algal blooms: how strong is the evidence that nutrient ratios and forms influence their occurrence? Estuar. Coast. Shelf Sci. 115 (2012) 399–413.

[48] A.M. Farag, T. May, G.D. Marty, M. Easton, D.D. Harper, E.E. Little, L. Cleveland, The effect of chronic chromium exposure on the health of Chinook salmon (*Oncorhynchus tshawytscha*), Aquat. Toxicol. 76 (2006) 246–257.