

ACHIEVERS JOURNAL OF SCIENTIFIC RESEARCH*Open Access Publications of Achievers University, Owo*Available Online at www.achieversjournalofscience.org**An Overview of Characterization and Treatment Methods of Wastewater from Iron and Steel Industries**Lawal, J.A.^{1*} and Anaun, T.E.¹¹Department of Chemical Sciences, Achievers University, Owo, Ondo State, Nigeria.

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Abstract

This paper reviews physicochemical characteristics of iron and steel industrial wastewater and the trend in development of treatment methods. The nature of wastewater generated largely depends on the raw materials, process operation, products and by-products. In coke-oven plants, toxic wastewater containing contaminants such as cyanide, ammonia, poly aromatic hydrocarbon, phenolic compounds and other complex organic compounds are generated. Wastewater generated from metal processing and metal finishing steel industries are in the form of spent pickle liquor and acidic rinse water containing contaminants such as metal salts, free acids and oil and grease. To tackle these diverse natures of iron and steel wastewater, different treatment methods and combination of compatible treatment techniques have been developed to handle specific type of steel industrial wastewater.

Keywords: Iron and Steel Industries; Wastewater; Coke-oven; Pickling; Treatment Techniques**1.0 Introduction**

The expansion of waste-intensive steel production processes has continued to be a source of global concern as a result of ever increasing deluge of toxic steel waste into the ecosystem with unprecedented negative impact on the environment. During manufacturing of steel and its derivative, many contaminants such as mineral acids, alkali, oil and grease, organic compounds and heavy metals are discharged and these alter the physicochemical properties of the receiving water bodies and the environment in general. The accumulation of these contaminants which often exceeds tolerable limits and which in most cases

are not tackled in a safe manner have resulted in pollution of soil, air and water bodies; leading to soil contamination, poor air quality, lack of access to safe water for human consumption and extinction of some fresh water aquatic species (Smol, 2012). To address the various forms of pollution emanating from steel industries, adoption of cleaner production technologies, waste minimization and treatment technique initiatives are being encouraged (Zhang *et al.*, 2007).

In steel manufacturing processes, high volumes of water is consumed for processes which include cooling of equipment through cooling panels, quenching, slag handling, coke-oven, acid pickling and metal finishing processes (Harika *et*

al., 2015). According to Beh *et al.* (2012), an average steel mill in Malaysia uses about 18,000 m³ of water per day. In a similar report (Strugariu and Hebut, 2012), 150 to 200 tons of water per ton of steel produced is consumed by an average steel plant. In general, wastewater discharged from steel industries differs in pollution load, concentration, characteristics, frequency of generation and flow. This is mainly determined by the nature of raw materials, types of process, by-product and efficiency of the operation system which varies from one steel industry to another. This diversity in the nature of steel effluents can be classified as; coke-oven, steel mills and metal finishing wastewater and their remediation calls for specific treatment technique and design of treatment plant (Lai *et al.*, 2009; Sharma and Philip, 2016).

2.0 Characteristics of Iron and Steel Wastewater

Iron and steel wastewater is basically generated from two major processes which are coke production and steel processing.

Table 1. Characteristics of Coke-oven Wastewater

Parameter	Ghose, 2002	Vazquez <i>et al.</i> , 2007	Maranon <i>et al.</i> , 2008	Habio <i>et al.</i> , 2010	Sharma & Philip, 2016
PH	ND	8.1	ND	ND	ND
Conductivity (ms/cm)	ND	7.1	ND	ND	ND
TSS (mg/L)	ND	32	ND	ND	ND
NH ₄ ⁺ -N (mg/L)	454.95	688	133 – 348	200-500	152
NO ₃ -N (mg/L)	462.76	76	ND	ND	ND
Phenol (mg/L)	10.3	207	100-220	250-350	ND
Cyanide (mg/L)	ND	32	11 – 41	ND	20
COD (mg/L)	ND	1100	800-1870	1700-2200	420
SCN (mg/L)	ND	267	198-427	ND	ND
BOD (mg/L)	ND	579	ND	ND	ND

ND: Not determined

2.2 Characteristics of Steel Processing Wastewater

Steel processing wastewater originates mainly from processes such as pickling, passivation, rinsing, enameling and electroplating which are associated with the use of acidic or alkaline solutions. Hydrochloric and sulphuric acids are

2.1 Characteristics of Coke-oven Wastewater

In coke-oven plants, natural coal is converted into coke for reduction of iron ore in a blast furnace. This process generates and releases by-product gases from the oven chamber at high temperature (Parimal and Ramesh, 2014). The cooling, washing and purification of the by-product, involves contacting with flushing liquor; a process that requires a large quantity of water resulting in generation of pollutant laden wastewater. Coke-oven plant wastewater is considered toxic because of presence of nitrogeous contaminants such as ammonium nitrogen (NH₄⁺-N), nitrate nitrogen (NO₃-N), thiocyanates (SCN) and aromatic compounds (Sinha *et al.*, 2014; Harika *et al.*, 2015). Coke-oven wastewater has equally been reported to contain low level of dissolved oxygen (DO), suspended solids (SS) high level of chemical oxygen demand (COD) and biological oxygen demand (BOD) (Shigeki *et al.*, 2010; Parimal and Ramesh, 2014). Physicochemical parameters of some coke-oven wastewater are presented in Table 1.

the most commonly used acids for surface treatments such as electrolysis, electroplating and acid pickling (Jeong *et al.*, 2005). The use of such acid in steel processing is the reason for the acidic nature of some steel wastewater (Jorge *et al.*, 2005; Anuradha *et al.*, 2013). The characteristics and frequency of wastewater discharge from steel processing industries depend on operation

sensitivities of the plant, metallic raw materials and by-products (Celalettin *et al.*, 2009). Effluents from this type of industries usually contain high concentration of total dissolved solids (TDS), sulphate and chloride ions and heavy metals such

as iron (Fe), copper (Cu), lead (Pb), nickel (Ni), aluminum (Al) and zinc (Zn) as presented in Table 2.

Table 2. Characteristics of Steel Processing Wastewater.

Parameter	Steel processing Lawal <i>et al.</i> , 2020a	Semi-conductor Wong <i>et al.</i> , 2013	Metal finishing Adakole and Abolude, 2009	Nickel electroplating Poonkothai and Vijayavathai 2015
pH	1.38	6.30	4.5	9.5
NTU	ND	727.7	ND	ND
EC (ms/cm)	9.82	0.241	ND	5.3
TSS (mg/L)	85.23	22.37	395	600
TDS (mg/L)	2219.32	ND	4348	3200
DO (mg/L)	5.19	3.98	ND	ND
BOD (mg/L)	97.30	31.51	ND	ND
COD (mg/L)	244.33	444.7	ND	1502
Chloride (mg/L)	2456.35	ND	823.87	2749
Sulphate (mg/L)	491.25	ND	1992.67	1449
Oil & grease (mg/L)	ND	ND	ND	28
NO ₃ -N (mg/L)	ND	ND	84.5	ND
Fe (mg/L)	235.64	3.0	ND	ND
Cu (mg/L)	ND	1.65	7.97	ND
Pb (mg/L)	10.84	ND	1.10	ND
Ni (mg/L)	ND	ND	11.85	126
Zn (mg/L)	38.22	ND	5.06	ND
Al (mg/L)	ND	2.33	ND	ND

3.0 Treatment Methods

3.1 Physical and Chemical Treatment Methods

Several techniques such as membrane separation, electrochemical techniques, adsorption, solvent extraction, advanced oxidation, neutralization/precipitation and other methods have effectively been used for treatment of coke-oven, steel processing and metal finishing wastewater.

3.1.1 Membrane Separation

A membrane is a thin layer of semi-permeable material that separates substances when a driving force is applied across the membrane. The principle is based on the fact that, if an anion exchange membrane is placed between two solutions having the same composition but

different concentration, then mass transfer through the membrane occurs (Tang *et al.*, 2006; Agrawal, 2009). Depending on the size of particles to be retained, various types of membrane filtration including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) have effectively been developed from different materials such as polymer (polyethylene, polyether sulfone, polypropylene), metallic and ceramics (Ersu and Ong, 2008; Santos and Judd, 2010) for remediation of iron and steel wastewater.

Extraction of various acids from waste solutions of steel wastewater from processes such as metal-refining, pickling of secondary steel products, aluminum foil etching and etching of stainless steel have been carried out using membrane filtration technique (Oh *et al.*, 2000; Takahashi and Kuchi, 2003). Chitosan-enhanced MF, low

cost ZnAl₂O₃-UF and polymer supported UF have been employed to achieve over 90 % removal of metals such from wastewater (Juang and Shiau, 2000; Saffaj *et al.*, 2004). Membrane filtration of cyanide from coke-oven wastewater have carried out at pressure of 13 Kg/cm² and flow rate of 700 liters per hour recorded 94 % removal (Ramesh *et al.*, 2011). Diffusion dialysis membrane has been utilized in the same operation with electro dialysis to increases the regeneration of H₂SO₄ and HCl for up to 80 % and rejection efficiency as high as 94 % of metal ions such as iron, nickel and vanadium across the membrane (Xu *et al.*, 2009; Wei *et al.*, 2010). Combined diffusion and electro dialysis technique working at flow rate of 0.6 L/(hm²) and current of 2.0 A at 0.41 kwh recovered HCl from aluminum smelt effluent at 74.9 %. (Zhang *et al.*, 2012).

Removal of organic contaminants such as polycyclic aromatic hydrocarbons, trihalomethanes and phthalates from coke-oven wastewater have been carried out using membrane filtration (Dudziak *et al.*, 2003; Marzena and Wlodarczyk-Makula, 2012). For dual-stage nanofiltration, pressure was found to be the most significant factor on water permeate flux and dissolved solids (Jie *et al.*, 2014). Incorporation of ultrafiltration on membrane filtration as a dual process in coke-oven wastewater treatment has been shown to greatly enhance polyaromatic hydrocarbon removal (Marzena and Wlodarczyk-Makula 2012).

3.1.2 Electrochemical Techniques

In electrochemical techniques such as electro dialysis (ED), electrocoagulation (EC) and electrodeposition, electric potential is applied as the driving force for the separation of ionized species in solutions. These techniques have successful been used for the removal of organic compounds and nitrogenous substances present in coke-oven wastewater (Zhang *et al.*, 2007; Yanli *et al.*, 2011). Electrocoagulation technique using iron as electrode have been employed to remove chromium from electroplating wastewater (Dermentzis *et al.* 2011). Removal of Cu²⁺, SO₄²⁻ ions and COD of an industrial electroplating rinse water has successfully been carried out using

hybrid electrochemical ion exchange (EIX) and electro-oxidation (EO) reactor (EIX-EO) (Meyyappan *et al.*, 2012).

3.1.3 Adsorption

Adsorption process has a wider industrial application including activated carbon, synthetic resins and water purification. The technique is currently considered to be very suitable for wastewater treatment because of its simplicity of operation and low-cost. Different materials such as activated carbon, natural and modified clays, carbon nanotubes, zeolite, fly ash and bio-adsorbent have successfully been utilized to remove contaminants from wastewater (Gupta *et al.*, 2003; Aman *et al.*, 2008; Fu and Wang, 2014). Modified biopolymer, synthetic zeolite magnetically modified with iron oxide, clay modified with polymeric materials and other chemically modified adsorbents have equally been developed for remediation of industrial wastewater (Nah *et al.*, 2006; Barakat, 2008; Solenera, 2008). Simultaneous adsorption of Ni²⁺ and Mn²⁺ ions from aqueous solution unto a Nigerian kaolinite clay has been reported (Dawodu and Akpomie, 2014). Modification of kaolinite clay with ammonium oxalate and sodium hydroxide has been utilized to increase adsorption of Fe²⁺, Pb²⁺ and Zn²⁺ ions from aqueous solution and steel processing wastewater (Lawal, *et al.*, 2020b; Lawal *et al.*, 2020c). In another report, adsorbent prepared from electric arc furnace slag effectively adsorbed iron and zinc from steel processing wastewater (Beh *et al.*, 2012).

3.1.4 Solvent Extraction

The technique involves extraction of soluble metal compounds from aqueous phase into organic phase which is then followed by purification or concentration using electrowinning and other methods to recover the metal. The solvent usually used as extractant can be an acidic, basic or neutral compounds with capacity to dissolve pollutants (Sinha *et al.*, 2014). Mahmoud and Barakat (2001), recovered and separated copper, chromium and zinc using solvent extraction and electrowinning techniques. Gupta *et al.* (2002), recovered chromium with Alamine and tri-n-butyl

phosphate from electroplating wastewater. Zinc has also been extracted from chloride solution using tri-n-butyl phosphate (Jose and Alguacil, 2001).

3.1.5 Advanced Oxidation Technique

Advanced oxidation process (AOP) is a separation technique that involves generation of highly reactive free electrophilic hydroxyl radicals which rapidly react with organic compounds. The removal of a hydrogen atom (aliphatics) or addition on an unsaturated bond (aromatics) initiate the radical oxidation chain reaction (Stasinakis, 2008). Several AOP such as Fenton's process, photo Fenton process, ozone/ultraviolet, H₂O₂ photolysis, electrochemical advanced oxidation processes and others have widely been used for degradation of recalcitrant organic contaminants (dyes, pesticides and herbicides, phenolic compounds, surfactants, drugs) in industrial wastewater (Barrera-Diaz *et al.*, 2014). In Fenton's process, the main steps involved are oxidation, neutralization, flocculation and sedimentation (Aydin *et al.*, 2002; Mahiroghu *et al.*, 2009) and the process has been found to be most effective in acidic condition (Kochany and Lipczynska-Kochany, 2009).

3.1.6 Neutralization/Precipitation

These processes are conventional method for treatment of wide range of industrial wastewater by neutralization through agitation and aeration with lime such as caustic soda, soda ash, calcium lime and ammonia. Calcium lime (CaO) is the most preferred precipitant, but a relatively high amount is required for effective precipitation (Chen *et al.*, 2009; Anuradha *et al.*, 2013). Precipitates of amphoteric metals, such as zinc and lead, tend to re-dissolve at certain pH, hence, pH must be strictly controlled. Aluminum chloride, ferric chloride and ferric sulphate have traditionally been used as coagulant for removal of pollutants (Baoyou *et al.*, 2007). To improve efficiency of coagulation process, synthetic and natural polymer can be added as aids/bioflocculant (Mingquan *et al.*, 2008; Verma *et al.*, 2012). A composite poly aluminum chloride was found to exhibited 30% more efficiency than conventional aluminum and ferric salts

(Mingquan *et al.*, 2008). Removal of metals from pickling liquor of a stainless steel by precipitation method has been investigated using three sequential precipitation methods (Dufour *et al.*, 2001). Precipitation at low pH value of 3 was first carried out to remove the total Molybdenum content as molybdenate. Modified precipitation consisting of two other stages were then carried out for the recovery of iron and chromium hydroxides and oxides, along with remnant molybdenate, which was then followed by recovery of nickel as hydroxide. Neutralization of leachates generated from spent pot-lining in a primary aluminum smelting process with the aluminum anodizing caustic by-product have successfully been used to recovered aluminum as solubilized fluoride acceptable to AlF₃ manufacturers (Lisbona *et al.*, 2012).

3.2 Biological Treatment Methods

Biological treatment is a low-cost technique for coke-oven wastewater treatment. Activated sludge is the most widely practiced method which involves decomposition and degradation of organic pollutants with the help of a dense microbial population while keeping the microbes in suspension with the wastewater under aerobic conditions (Parimal and Ramesh, 2014). Activated sludge process have been complemented with chemical oxidation, membrane filtration and other techniques to improve biodegradation ability and shortening retention time (Cui and Jahng, 2004; Khanal *et al.*, 2007).

3.2.1 Single-Step Activated Sludge System

In single-step system, the activated sludge is built up on a single aerated reactor which is then followed by sedimentation. Biological treatment by activated sludge of a steel coke-oven wastewater was investigated using a single step process to define the condition and restrictions for nitrification of ammonia-nitrogen and to determine the extent of denitrification efficiency (Stig *et al.*, 2012). From the results, high concentrations of ammonia-nitrogen and complex nitrogen compounds such as cyanide and thiocyanate reduced significantly after an

acclimatization period. Less than 40 days solid retention time was required to establish a stable nitrification at mesophilic temperature of 25 to 30 °C. A complete denitrification was found possible as long as the concentration of organic carbon in the coke-oven wastewater is sufficient. Chakraborty *et al.* (2010), studied biodegradation of phenol using native bacteria strains isolated from coke-oven processing wastewater. One of the strains found to be highly effective for the removal of phenol, was used as sole carbon and energy source. The results obtained show that concentration of phenol reduced significantly from 200 to 79.84 mg/L.

3.2.2 Multi-step Activated Sludge System

Multi-step system processes of degrading pollutants involving different step-wise conditions such as anoxic, aerobic and anaerobic (Kim *et al.*, 2009). In anoxic-oxic conditions, heterotrophic denitrifiers convert nitrite and nitrate into nitrogen gas using organic carbon sources as energy provider and electron donor for the denitrification reaction (Wang *et al.*, 2019).

A laboratory-scale treatment of industrial coke wastewater was studied using a three step process sludge system (Maranon *et al.*, 2008). Nitrate removal was carried out as the first step, followed by biodegradation of phenol and SCN by anoxic-oxic step accompanied by oxidation of $\text{NH}_4^+\text{-N}$ to nitrate and finally separation of nitrification.

Biodegradation of SCN was found to greatly improve the efficiency of the process than when carried out simultaneously with nitrate removal. From the results, 99 %, 97 %, 63 %, 98 % and 90 % were achieved for phenol, SCN, COD, $\text{NH}_4^+\text{-N}$ and total nitrogen (TN) removal.

Sequencing Batch Reactor (SBR) is another multi-system activated sludge technique that has been used to degrade contaminants in coke-oven wastewater. This process is a sequential activated sludge batch reactor with aeration and sludge settlement, both occurring in the same tank (Papadimitriou *et al.* 2009). Biofilm multi-step technique have also been utilized to decrease the amount of COD and $\text{NH}_4^+\text{-N}$ at removal efficiency of 92.3 % and 97.8 % respectively under hydraulic residence time of 116 hours (Xin *et al.*, 2014).

3.3 Advantages and Limitations of Different Methods of Treating Iron and Steel Wastewater

Over the years, different wastewater treatment techniques have been designed, modified and complemented to ameliorate the environmental impact of industrial wastewater and to overcome the limitations of the existing methods at minimal cost. However, all the methods designed so far, have suffered from some form of limitations (Table 3).

Table 3. Advantages and Disadvantages of Various Iron and Steel Wastewater Treatment Methods

Method	Advantages	Disadvantages	Reference
Membrane separation	Applicable for wide range of pollutants, compactible with other techniques.	Expensive, membrane fouling.	Yuefei <i>et al.</i> , 2011
Electrodialysis	Small amount of sludge is generated, compactible with other techniques.	Energy consumption is high, membrane fouling.	Mohammed <i>et al.</i> , 2005
Adsorption	Inexpensive, simple to operate.	pH dependent, efficiency depend on the type of adsorbent and nature of pollutant.	Lawal <i>et al.</i> , 2020b
Neutralization	Low cost and simple to operate.	pH dependent, poor settling ability.	Verma, <i>et al.</i> , 2012;
Solvent extraction	Selective recovery of metals, compactible with other technique.	Ineffective for high metal concentration, low loss of solvent	Sinha <i>et al.</i> , 2014
Advanced oxidation	Low energy consumption.	Effective only within acidic pH.	Stasinakis, 2008
Activated sludge (single-step)	Compactible with other techniques,	High amount of sludge is generated, poor settling ability,	Kumar <i>et al.</i> , 2003
Multi-step activated sludge	Small amount of sludge is generated.	Loss of active biomass.	Lin <i>et al.</i> , 2013

4.0 Conclusion

From the review, all methods for treating iron and steel wastewater are effective in some forms, but the presence of some contaminants can limit their potential. To overcome the limitations, compatible techniques have been integrated as dual or multi-step complementary method of treatment.

Biological treatment process is a low-cost method of treatment of coke-oven wastewater, but poor settling of sludge, inhibition of bacteria activity by high concentration of cyanide and the presence of other recalcitrant substances are the major limitation associated with activated sludge biological process. However, the incorporation of multi-step bio-technique and some compatible membrane separation techniques have helped to overcome the challenges.

Neutralization/precipitation is one of the low cost technique employed for the treatment of steel and metal finishing wastewater, but production of excessive sludge is its major disadvantage. In order to improve the performance, the process has been integrated with other methods. Concurrent running of electrodialysis and diffusion dialysis for recovery of metals from spent pickle liquor complements each other as dual technique. This is made possible because diffusion dialysis flow rate is compatible with electrodialysis current; and their integration was found to be cost-effective and environmental friendly. The utilization of solvent extraction process can help achieve nearly 100% recovery of metal from wastewater, but the method is associated with slow separation process and loss of solvent.

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