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Potential valorisation of ferrous slag in the treatment of water and wastewater: A review

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Abstract. The generation of ferrous slag, an industrial by-product from the iron ore industry, results in serious environmental problems. The chemical compositions indicate 30-34% SiO_2, 30-34% CaO, 18-22% Al_2O_3 and 0.5-0.6% Fe_2O_3. The specific gravity, moisture content and pH are in the range of 1.3-1.65, 9.1-10% and 8.5-9.0 respectively. The major part of the slag is composed of sand-size particles. The problems of disposal of slag could be minimized by considering its use in various environmental engineering applications providing additional value to the by-product. This paper mainly focuses on the potential utilization and valorisation of ferrous slag in both water and wastewater treatments. It is effective for the treatment of water and wastewater containing nutrients, heavy metals and polluted river/stormwater.

Keywords: blast furnace slag; nutrient removal; heavy metals; filter media

1. Introduction

The blast furnace slag is a solid waste produced from the iron industries and hence the major challenge facing such industries is the disposal of huge quantities of ferrous slag. It results in the degradation of land, surface and groundwater contamination besides the aesthetic appearance of the nearby areas of the industries. The effect of the impact is long term and is a major challenge facing the surrounding environment. Nowadays the blast furnace slag is not considered as a waste material whereas it could be viewed as a by-product which finds its potential reuse as a source of fine aggregate in place of natural river sand (Asish *et al*. 2016, Patra and Mukharjee 2017, Patra and Mukharjee 2018). Since over-exploitation of river sand ultimately results in the ecological imbalance of the environment, slag can be utilized in place of sand for various environmental engineering applications. Now, the blast furnace slag has found potential uses like treatment of acid mine drainage, stabilization of sewage sludge and organic soil, polluted sources of water and wastewater which contain nutrients and heavy metals and hence is not considered a waste (Oguz

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2004, Kietlińska and Renman 2005, Riefler 2007, Hallberg and Renman 2008, Nehrenheim *et al*. 2008, Kaya 2016, Anjali *et al*. 2019).

There are various types of adsorbents for phosphate, nitrate and heavy metals. Mercado-Borrayo *et al*. (2018) describe the practice of using iron slag as sorbents or reagents for the co-precipitation of contaminants. The by-products of industries can be used as adsorbents for removing nutrients and heavy metals from water and wastewater (Singh *et al*., 2018, Yasipourtehrani *et al*., 2019). *Gao et al.* (2017) investigated the adsorptive ability of treated water quenched blast furnace slag in three different forms for eliminating methyl orange from aqueous solutions. Although there are different techniques for removing heavy metals, adsorption and ion exchange processes are preferred due to its high efficiency and low cost (Naushad, 2014, AL-Othman *et al*., 2012).

2. Blast furnace slag

During the production of iron, one of the major by-products generated from the blast furnace is ferrous slag (Lim *et al*. 2016). In general, blast furnace slag production ranges from about 300-540 kg per tonne of pig or crude iron from an ore feed containing 60 to 65% iron. It has been estimated that around 10 million tonnes of blast furnace slag per year are generated in India from iron and steel industry (Indian Bureau of Mines 2018), about 0.50 and 0.25 million tonnes of blast furnace slag is produced by Svenskt Stål AB in Oxelösund and Luleå in Sweden (Johansson 2010) and about 19.5 and 4.7 million tonnes of granulated and air-cooled slag are annually generated in Japan (Isawa 2013) and about 346 kg/t hot metal in China (Li and Guo 2014).

The blast furnace slag is defined as a non-metallic product consisting essentially of silicates and alumina-silicates of calcium and other bases formed in a molten condition along with iron in a blast furnace (IS: 12089 1987, Lewis 1982). The blast furnace is charged with sources of iron oxide (ores, pellets, sinter, etc.), flux stone (limestone and dolomite) and fuel (coke) at a temperature of about 3000°C to produce pig iron. In this process, slag is generated as a by-product. It consists of the impurities from iron ore such as silica and alumina combined with calcium and magnesium oxides from the flux stone along with small amounts of sulphur and ash. Thus it indicates the presence of calcium, magnesium, manganese and aluminium silicates and a combination of all these components. The blast furnace slag also contains beryllium, total chromium, manganese, molybdenum and selenium, only a little above the general soil concentrations. The chemical composition of blast furnace slag generated from Indian steel industries and worldwide is given in Tables 1-2 respectively. The important physical properties of slag are grain size, density, porosity and hydraulic conductivity and are listed for different types of slag in Table 3.

The physical and chemical composition of ferrous slag varies depending upon the places or sources of generation, the temperature at the time of water quenching and the process changes/ different methods of operations or the changes in methodologies involved (Korkusuz *et al*. 2007). The SiO_2 and CaO values were found to be high, followed by Al_2O_3 as shown in Table 2. The iron content is around 0.5% in blast furnace slag (Indian Bureau of Mines 2018). The leachate from the slag may be alkaline due to its calcium and magnesium contents (O'Kelly 2008).

The ferrous slag is cooled for making different types of slag namely air-cooled slag, granulated slag and expanded slag. Air-cooled slag is produced by allowing the molten slag to cool slowly in a pit under atmospheric conditions. During this process, escaping gases make it porous and cellular

Table 1 Chemical composition of blast furnace slag generated in Indian steel plants (Indian Bureau of Mines 2018)

Name of plant	SiO_2 (%)	Al_2O_3 (%)	CaO (%)	MgO (%)	MnO (%)	FeO (%)	Sulphur (%)
Bhilai Steel Plant, Durg, Chhattisgarh	34.52	20.66	32.43	10.09	0.23	0.57	0.77
Bokaro Steel Plant, Bokaro, Jharkhand	30.06 - 31.85	21.12 - 22.71	32.48- 34.17	10.12- 10.39	-	0.26 - 0.37	-
Rourkela Steel Plant, Rourkela, Odisha	34.38 - 34.85	17.82 - 20.91	32.99- 34.26	9.29- 9.68	0.07- 0.12	0.46 - 0.58	0.47 - 0.61
Durgapur Steel Plant, Durgapur, West Bengal	32.68	21.23	32.14	-	-	-	-
Visvesvaraya Iron and Steel Plant, Bhadravati, Karnataka	32.00	18.00	33.00	9.00	-	0.50	-
IISCO Steel Plant, Burnpur, West Bengal	32.60	23.30	33.70	7.60	-	-	-
Rashtriya Ispat Nigam Ltd., Visakhapatnam, Andhra Pradesh	35.33	16.60	36.89	8.48	0.12	0.51	-
IDCOL, Kalinga Iron Works Ltd., Barbil, Odisha	33.00 - 34.00	24.00 - 25.00	29.00 - 30.00	8.00 - 9.00	0.50 - 0.60	0.70 - 0.80	1.00
Tata Steel Ltd., Jamshedpur, Jharkhand	34.50	20.80	34.30	7.30	0.052	0.60	-
JSW Steel Ltd., Bellary, Karnataka	35.20	19.00	34.90	8.76	0.14	0.039	-
Visa Steel Ltd., Kalinganagar, Odisha	33.80	15.39	35.38	10.25	0.64	0.74	0.92
Neelachal Ispat Nigam Ltd., Kalinganagar, Odisha	32.62	32.62	33.25	9.91	0.40	0.55	0.62

Table 2 Chemical composition of slag in literature

Type of Slag	SiO_2 (%)	Al_2O_3 (%)	CaO (%)	MgO (%)	MnO (%)	FeO (%)	Sulphur (%)	References
Blast Furnace Slag	32.00 to 42.00	7.00 to 16.00	32.00 to 45.00	5.00 to 15.00	0.20 to 1.00	0.10 to 1.50[a]	1.00 to 2.00	Lewis (1982)
Blast Furnace Slag	35.00	14.00	41.00	7.00	nm[c]	nm[c]	0.80	Environment Agency UK (2007)
Blast Furnace Slag	37.14	9.15	37.40	11.70	nm[c]	1.05[a]	0.37[b]	Das *et al.* (2007)
Granulated Slag	32.20	14.90	43.00	5.26	0.34	0.53[a]	1.98[b]	Hizon-Fradejas *et al.* (2009)
Air-cooled Slag	30.60	15.5	42.00	7.19	0.30	0.38[a]	1.97[b]	
Blast Furnace Slag	33.26	15.63	38.69	9.41	nm[c]	0.83	0.35[b]	Gong *et al.* (2009)
Crystalline Blast Furnace Slag (Oxelösund)	34.00	13.00	30.00	16.50	0.60	0.50	1.00	Johansson (2010)
Crystalline Blast Furnace Slag (Luleå)	33.00	12.50	32.50	16.50	0.30	0.20	1.10	
Blast Furnace Slag	39.56	10.82	37.68	6.79	nm[c]	0.33[a]	-[d]	Oguz (2004)
Fine Amorphous slag	35.30	9.30	35.00	13.70	0.40	0.36	nm[c]	Johansson and Gustafsson (2000)
Coarse Amorphous slag	35.50	9.60	35.00	13.70	0.41	0.34	nm[c]	

Table 2 Continued

Type of Slag	SiO_2 (%)	Al_2O_3 (%)	CaO (%)	MgO (%)	MnO (%)	FeO (%)	Sulphur (%)	References
Fine Crystalline Slag	35.10	10.60	33.70	14.40	0.47	0.43	nm[c]	Johansson and Gustafsson (2000)
Coarse Crystalline Slag	35.20	11.40	33.40	14.30	0.47	0.43	nm[c]	
Blast Furnace Slag	21.82	16.9	37.82	5.53	nm[c]	13.1[a]	nm[c]	Ge *et al.* (2015)
Blast Furnace Slag	33.2	13.2	30.10	16.40	0.50	0.30[a]	1.10	Hallberg and Renman (2008)
Granulated Blast Furnace Slag	36.00	10.00	39.00	nm[c]	nm[c]	0.50[a]	nm[c]	Agrawal *et al.* (2011)
Blast Furnace Slag	36.11	8.46	36.23	3.14	nm[c]	0.63	nm[c]	Lu *et al.* (2008)

[a] as Fe_2O_3, [b] as SO_3, [c] nm not mentioned, [d] as Sulphide (S^{2-}), [e] as FeO_3, [f] as iron compounds

Table 3 Physical properties of blast furnace slag

Type of Slag	Grain size (mm)	Density (kg/m^3)	Porosity (%)	Hydraulic Conductivity (m/day)	References
Fine Blast Furnace Slag	0.5-2.0	1245	55	1990	Hedström and Rastas (2006)
Coarse Blast Furnace Slag	1.0-5.6	1158	54	4260	
Blast Furnace Slag	0.5-4.0	2200	28	255	Nilsson *et al.* (2013)
Amorphous Slag Coarse	0.25-4.00	nm[b]	46.7	40.6	Hylander *et al.* (2006)
Crystalline Slag Coarse	0.25-4.00	nm[b]	45.5	15.9	
Crystalline Slag Very Coarse	2.00-7.00	nm[b]	50.9	4950	
Fine Amorphous Slag	nm[b]	1380	55	3.2	Johansson and Gustafsson (2000)
Coarse Amorphous Slag	nm[b]	1500	44	40.6	
Fine Crystalline Slag	nm[b]	1610	45	0.8	
Coarse Crystalline Slag	nm[b]	1600	40	15.9	
Granulated Blast Furnace Slag	200-2.80	1300-1500	nm[b]	nm[b]	Agrawal *et al.* (2011)

[b] nm not mentioned

or vesicular structure resulting in low density. The unique physical properties such as porosity and cellular structure have found its suitability for several applications. Under controlled cooling, the slag becomes hard and dense and finds applications in landfills (Indian Bureau of Mines 2018). Granulated slag is a glassy granular product processed by rapid chilling or quenching of molten slag with high-pressure water jets or steam and air or a combination of water and air. It is found useful for drainage works and soil conditioning for the growth of plants and microbes (IS: 12089 1987, Lewis 1982). Expanded slag is formed by controlled cooling of molten slag with water or water with a combination of steam and compressed air. It has high porosity and vesicular nature compared to air-cooled slag.

3. Valorisation of ferrous slag

The best waste management practices could be achieved by reusing the slag in technically feasible and commercially suitable applications. The high pH could be attributed to the presence of free lime, iron and calcium silicates (Bowden *et al.* 2006). Pre-treatment is sometimes necessary to eliminate impurities which depend on the characteristics and possible utilization areas of slag (Environment Agency UK 2007). Its vesicular nature and mineralogical properties find its suitability as a barrier material against heavy metal contamination from landfill sites.

The role of ferrous slag in water and wastewater treatment is manifold. It has a significant role in pollutant removal (Ge *et al.* 2015). The iron slag, due to highly alkaline pH, can be applied for neutralizing acidic wastes and mine drainage, agricultural uses such as remineralization and conditioning of soil, as a liming agent, fertilizer, etc (Proctor *et al*. 2000). Several studies have demonstrated that it could be used as media for removing nutrients (Johansson 2010, Oguz 2004, Johansson and Gustafsson 2000, Hedström and Rastas 2006, Korkusuz *et al*. 2007, Ballantine and Tanner 2010, Shilton *et al*. 2013). Hedstrom and Rastas (2006) and Westholm (2010) described phosphorus sorption capacity of slag from wastewater. The earlier research was mainly done for removing phosphate from synthetic wastewater (Oguz 2004). Johansson and Gustafsson (2000) suggested further research on nutrient uptake by plants and its use as fertilizers while conducting studies on different media such as blast furnace slag and opaka (50% $CaCO_3$, 40% SiO_2 and 10% Al, Fe and other oxides). Phosphorous recycling was also possible by growing barley seeds in mixed media consisting of blast furnace slag, limestone, polonite, opaka and sand (Hylander *et al*. 2006) and reed beds planted with *Phragmites australis* in composite media using gravel, blast furnace slag and sand (Korkusuz *et al*. 2007). Thus it is obvious that phosphate removal from wastewater could be achieved using either blast furnace slag alone or in combination with other materials such as hydrated lime as pointed out by Gong *et al*. (2009). Nilsson *et al*. (2013) compared the removal of phosphorous and bacteria using polonite and blast furnace slag separately.

There are several treatment technologies for removing heavy metals from industrial wastewater, including cation exchange materials (Naushad *et al.*, 2013, Naushad, 2014, Naushad, AL-Othman, 2015 and Carolin *et al*. 2017). The blast furnace slag could be used for eliminating heavy metals such as copper, zinc and nickel (Dimitrova *et al*. 2000) and a combination of these metals along with cadmium and chromium from wastewater. It would be effective if pre-treatment is given to remove suspended solids (Hallberg and Renman 2008). Crystalline and amorphous blast furnace slag along with pine bark of size 0.0025-0.01 m were used for column studies for removing copper, zinc and nickel. It was found that pine bark was more stable with respect to metal sorption than slag (Nehrenheim *et al*. 2008). The study conducted by Nehrenheim and Gustaffon (2008) showed its efficiency as a sorbent for nickel, zinc, lead, and chromium at higher concentrations which is in contrast to the previous study. Apart from the pure form, an activated slag has been made and used as a filter media for removing lead and chromium (Srivastava *et al.* 1997).

Wetlands are well known for their effective wastewater treatments. High BOD and suspended solids could be removed using a bed containing sand, gravel, organic matter and minerals (Karczmarczyk 2004). The application of slag in constructed wetlands makes a low cost and energy-efficient technology (Korkusuz *et al*. 2004).

The factors influencing the operation of various treatments and in the design of filters using slag are particle size (Nilsson *et al*. 2013), pH (Johansson and Gustafsson 2000, Ge *et al*. 2015, Srivastava *et al*. 1997), porosity (Korkusuz *et al*. 2007), hydraulic conductivity (Calder *et al*. 2006) and calcium content (Korkusuz *et al*. 2007) of the media, pH of wastewater (Oguz 2004, Nilsson *et al.* 2013), agitation rate in the reactor (Oguz 2004), temperature (Oguz 2004, Srivastava *et al.* 1997) and hydraulic retention time (Nilsson *et al*. 2013, Shilton *et al*. 2013, Srivastava *et al*. 1997).

4. Discussion on the reuse of slag

4.1 Removal of nutrients

The untreated disposal of sewage, overuse of fertilizers, detergents, stormwater runoff, animal husbandry, etc. contribute surplus amounts of nutrients in water bodies. The accumulated nutrients may enhance the eutrophication phenomenon. The blast furnace slag prevents eutrophication by making phosphorus insoluble in water and absorbs a part of the insoluble phosphorus (Horii *et al*. 2013). Its suitability as filter media has gained much attention recently since it has all the properties of efficient media.

The reaction of slag, which is rich in calcium and minor amounts of iron, with phosphate ions form complexes and precipitates out. The phosphorus removal is mainly contributed by precipitation phenomena. At low pH conditions, it might be due to ion exchange process (Lu *et al*. 2008). Fine amorphous and crystalline slag and coarse crystalline slag were found to be efficient for removing small amounts of phosphorous according to the study conducted using fine and coarse amorphous and crystalline slag and opoka (Johansson and Gustafsson 2000). However, fine amorphous slag showed its ineffectiveness at high phosphorus concentrations. Coarse amorphous slag and opoka were least efficient retainers of phosphorus. A decline in pH with phosphorous accumulation was also recorded. It was reported that phosphorus might be removed by adsorption or precipitation in the form of calcium phosphates. It was also supported by Johansson (1999), Lu *et al*. (2008) and Blanco *et al*. (2016). The suspended phosphorous can also be removed by filtration and precipitation along with other suspended solids. The slag has a high affinity of phosphates due to its porosity and results in dissolved total-P removal. The calcium released from the slag reacted with phosphate-phosphorous to form precipitates such as tricalcium phosphate, octacalcium phosphate and hydroxyapatite as indicated by Ge *et al*. (2014) which was also highlighted earlier by Korkusuz *et al*. (2007). The high content of calcium oxide produces several calcium phosphates which promote an increase in the phosphorus removal rate.

The experimental results for phosphate removal from synthetic wastewater in a batch reactor showed more than 99% efficiency (Oguz 2004). The minimum dosage of blast furnace slag was 60 g/L, for removing 180 ppm phosphate in 50 ml wastewater. In order to remove phosphate from aqueous solution at a temperature of 25°C and 45°C, a contact time of 20 min was adequate. In the adsorption process, the critical controlling parameters were agitation rate, temperature and pH of the aqueous solution. Hedstrom and Rastas (2006) conducted experiments using blast furnace slag for the treatment of wastewater and synthetic phosphate solutions. The sorption capacity was about 1493, 821 and 380 mg Total-P/kg fresh blast furnace slag and 638, 563 and 321mg Total-P/kg weathered blast furnace slag both at an initial phosphorus concentration of 20 mg/L, 10 mg/L and 5 mg/L respectively. The corresponding values for filtered wastewater and phosphorus spiked showed 176, 38 mg Total-P/kg fresh blast furnace slag at an initial phosphorus concentration of 4.2 mg/L and 0.75 mg/L respectively. The phosphorus sorption depends on the amount of dissolved calcium which is also proved later by Ge *et al.* (2014). It was preferred to use either fresh slag, which is in unison with the suggestions of Westholm (2010) or properly stored slag without exposure to atmosphere for wastewater treatment. Otherwise, the properties would be altered by leaching out the dissolved calcium. According to Hedstrom and Rastas (2006), the sorption capacities of blast furnace slag were considerably lower for real wastewater compared to the synthetic phosphate solutions and it is in concurrence with the findings of Oguz (2004) wherein the efficiency was above 99%. Yasipourtehrani *et al*. (2019) showed that the optimum adsorbent dose and contact time for phosphate removal using blast furnace slag was 60 g/L and 1 hr respectively.

The removal of phosphorus is difficult in subsurface flow wetlands with sand, gravel and improved site soil and hence there is a need for alternative media (Karczmarczyk 2004). The slag based wetland system was found to be efficient for removing phosphate phosphorus, Total-P, total suspended solids, coliform bacteria and COD from domestic wastewater and also for nitrate-nitrogen production or nitrification (Korkusuz *et al*. 2004, Korkusuz *et al*. 2005). Calder *et al*. (2006) suggested the need for field trials in wetlands for phosphorus sorption to validate the laboratory data. The study observed that hydraulic conductivity is an important parameter in determining the removal of phosphorus. Later Korkusuz *et al*. (2007) carried out field application studies for assessing the suitability of the media. The experiments were conducted on domestic wastewater with primary treatment and were applied to a wetland of 30 m^2 consisting of gravel as the bottom layer, blast furnace granulated slag as an intermediate layer and sand as the top layer. The wetland was planted with *Phragmites australis* and domestic wastewater was applied at a hydraulic rate of 100 mm per day. Prior to the field application, batch scale experiments for phosphorus sorption capacity were conducted on standard phosphorus solutions. It was found that it could be used to enhance the longevity of media in field applications. The sorption capacity varied between 0 and 9150 mg P per kg for initial phosphorus concentrations of 0-320 mgL^{-1}. Even at high loading rates, it could remove both phosphate-phosphorus and total phosphorus effectively. It might be due to its high values of calcium and porosity compared to other filter materials. Similar studies were conducted by Westholm (2010) and obtained better efficiency of about 95-100% in laboratory studies while it was only 40-53% for field trials. It was in contrast to the study by Valero *et al*. (2009) wherein the performance was higher for pilot scale filter in the field than bench scale filter in the laboratory.

Besides phosphorous, removal of other parameters such as total organic carbon and bacteria, *Enterococci* were possible using blast furnace slag (Nilsson *et al*. 2013). Column experiments performed for high and low BOD_7 values, 120 mg/L and 20 mg/L (mean) for an average hydraulic residence time of 535 hours showed 22% and 18% phosphorous removal, 21% and 19% TOC removal and 81% and 16% bacteria removal respectively. The blast furnace slag with high BOD had a more sorption rate than that with low BOD. The pH of wastewater, the particle size of filter, hydraulic retention time and organic loading rate influence the sorption behaviour and hence could have a role in the efficiency of filter media for phosphorus and TOC removal. It was therefore suggested to give pre-treatment to reduce the concentration of organic material. Feng *et al*. (2012) reported that water quenched slag particles provide proper environmental conditions for the growth of nitrifying bacteria. In a study on effluent from a waste stabilization pond using a filter column filled with slag, phosphorus removal was declined logarithmically with hydraulic retention time (Shilton *et al*. 2013). Removal efficiencies of 90% and 80% were achieved during experiments with real and synthetic phosphate solution in retention periods of 70 and 30 hours respectively. It was evident that removal efficiency was high in the case of stabilization pond effluents whereas synthetic phosphate solution marked a low value due to the high initial concentration of phosphorus. The high efficiency was contributed by the presence of oxidized iron compounds, cations, algae and other humic complexes in effluents. This study confirmed the role of iron oxyhydroxides and calcium carbonate in adsorption which was also stated by Pratt *et al.* (2007) and Haynes (2015). The maximum sorption ratio was 1.23 kg Total-P per tonne of slag. The weathered slag was capable of removing phosphorous better than fresh slag which was in contradiction with Hedstrom and Rastas (2006). Zuo *et al*. (2018) noticed a decrease in phosphorus removal efficiency from 100 to 6.6% due to the inhibition of Ca-P precipitation caused by the presence of dissolved organic carbon. The main drawback observed in the media is physical clogging due to the settlement of organic solids and other solids and may ultimately affect the hydraulic conductivity of media. Among the various parameters affecting the operation of the filter, the hydraulic retention time is to be considered as an important parameter since it gives an idea about the replacement of filter and the degree of treatment required for effluent.

Melter slag, which is produced during the conversion of iron sand into melter iron, due to its highly vesicular nature could be used as a filter media (Pratt *et al*. 2007). The media lasted for five years and durability could again be maximized by even more exposure to wastewater. After five years of successful operation, the media was regenerated by drying, agitation and crushing of the melter slag (Pratt *et al*. 2009). Crushing was the most efficient method of regeneration among other methods, but it could last only for two months. Moreover, periodic replacement of media and possible recovery were also mentioned by Kietlińska and Renman (2005) while conducting the treatment of landfill leachate. The results of the study conducted by Lu *et al*. (2008) indicated strong bond between slag particles and adsorbed phosphate preventing further desorption of phosphorus. The pH played a significant role in the rate and mechanism of removal. It was observed in the study that phosphorus removal was by chemical precipitation when pH raised above 8, by adsorption when pH was below 6 and by ion exchange and precipitation when pH in the range of 3 to 8.5. The chemical precipitation could recover or regenerate the exhausted filter media by stripping phosphorus from it (Pratt *et al.* 2011). Long term monitoring of active slag filter removed 77% of the Total-P initially and during first five years, its mean concentration in the effluent was 2.3 mgL^{-1} and removal was 19.7 tonnes and increased to 22.4 tonnes by the end of eleventh year (Shilton *et al*. 2006). The maximum phosphorus retention ratio was 1.23 kg Total-P per tonne of slag. The results proved that media replacement was required only after half a decade. Higher efficiency was also reported for real effluent than synthetic phosphate solution due to the difference in phosphate concentrations and the presence of dissolved and particulate constituents in the real effluent.

Gong *et al*. (2009) conducted batch experiments for phosphorous adsorption but it was very less for the combination of blast furnace slag-hydrated lime than hydrated lime alone. The suitability of granulated blast furnace slag, cement kiln dust, zeolite, coconut shell and silica sand for phosphorus sorption was studied by Agrawal *et al*. (2011a). But it was later observed while treating drainage water that a filter bed comprising of these materials was not competent for removing phosphate and pesticides like mefenoxa and propiconazole, whereas it could efficiently remove chlorothalonil from wastewater (Agrawal *et al*. 2011b).

4.2 Removal of heavy metals

The adsorption of heavy metals may be in the form of external diffusion on the particle surface and pore diffusion into the internal sites of the adsorbent. According to Nehrenheim and Gustafsson (2008), slag could act as a sorbent for nickel, zinc, lead and chromium ions at higher concentrations. The column study conducted by Hallberg and Renman (2008) for removing total and dissolved metals present in road runoff performed effectively. The removal of total cadmium was above 99%, zinc above 93%, copper 71-88%, nickel 40-69% and chromium 18% and dissolved cadmium and zinc over 90%, copper 77-86%, nickel 44-72% and chromium 6% respectively. Nevertheless, the effect of dissolved salt like sodium chloride present in road runoff could have an impact on removing total and dissolved metals. However, the removal of total cadmium was much affected at lower and higher salt concentrations. The ungranulated and thermally treated slag achieved more than 99% reduction for copper and the sorption was mainly due to the ion exchange mechanism and dependent on the calcium ion concentration (Dimitrova and Mehanjiev 2000). It was concluded that crystalline slag has more sorption rate than amorphous slag.

Srivastava *et al*. (1997) developed an activated slag filter by conducting batch experiments for the sorption of lead and chromium and studied various factors affecting the sorption such as pH, sorbent dosage, the concentration of adsorbate, presence of other metal ions, temperature and contact time. The adsorption followed Freundlich and Langmuir models and its performance was comparable to those of activated carbon. The uptake of lead was possible using slag and was recovered by chemical regeneration. Pratt *et al*. (2009) also regenerated the used melter slag in the same manner. When the dosage varied from 5 to 10 gL^{-1} the sorption was more. No significant removal was noticed at a higher dosage. Besides, an increased amount of adsorbent decreased the half-life of the sorption process. The influence of other metal ions reduced the uptake of chromium and lead in the presence of surfactant and the reduction was only 1.5% and 5.3% respectively. The process of adsorption was endothermic and the rate of removal increased with increase in temperature. The amounts of lead and chromium adsorbed in first hour at temperatures 30, 40 and 50 (±1°C) were $1x10^{-4}$, $1.23x10^{-4}$ and $1.30x10^{-4}$ $molg^{-1}$ and $0.77x10^{-5}$, $0.88x10^{-5}$ and $1.00x10^{-5}$ $molg^{-1}$ respectively. The sorption capacity was 50 to 80% after 1 hour contact time. The adsorption capacity of blast furnace slag for heavy metals such as lead, copper, cadmium, chromium and zinc varied from 4.3- 5.2 mg/g. The highest adsorption capacities were recorded by lead, copper and cadmium followed by chromium and nickel (Nguyen *et al*. 2018). Alkali activated slag was found effective for the immobilization of Cr (VI) which finds its application for the treatment of Cr (VI) bearing wastes (Zhang *et al*. 2017).

Separate column studies were conducted using crystalline and amorphous blast furnace slag along with sand and pine bark for copper, zinc and nickel removal (Nehrenheim *et al*. 2008). A longer retention time of 90 min increased the sorption rate of pine bark more stable concerning metal sorption than slag. The slag filter attained 35% accumulation of suspended solids similar to that of sand. Nehrenheim and Gustaffon (2008) found that sorption was higher for slag than pine bark at short contact time. At higher concentrations, slag was an efficient sorbent for nickel, zinc, lead, and chromium.

4.3 General water and wastewater treatments

The performance evaluation of a roughing filter consisting of blast furnace slag yielded 63%, 55%, 69%, 72% and 71% removal for chlorophyll ‘a’ content, green algae, blue-green algae, diatoms and total algal count respectively (El-Taweel and Ali 2000). Total bacterial count at 22°C and 37°C were 71% and 60% respectively and the removal of total coliform, faecal coliform, faecal streptococci, yeasts, *Candida albicans* were 59%, 55%, 55%, 69% and 56% respectively. The percentage removal of turbidity was above 80% in the roughing filter and above 90% in the slow sand filter. The above results depicted a substantial reduction of microorganisms and turbidity whereas poor performance was recorded for other physico-chemical parameters. It was further supported by Nilsson et al. (2013). Turbidity and iron removal using the roughing filter were 37% and 57% respectively. Abdolahnejad *et al*. (2014) studied the water softening behaviour of low sand filter using Iranian natural zeolite and blast furnace slag and showed better results. Similar to previous studies, adsorption had a critical role in removing turbidity. The cation exchange capacity of slag was 6.3 which represents a value between that of natural zeolite and sand. The slag modified filter showed 98.98% turbidity removal, 51.95% hardness removal. The mean EC reduction was 11.02%. Anjali *et al*. (2019) showed that a laboratory filter made of granulated blast furnace slag could completely remove turbidity, total suspended solids and colour from a synthetic influent containing 28.26 NTU, 128.85 mg/L and 177.05 PCU respectively at 0.32 m^3hr^{-1} m^2. Furthermore, the effect of increasing the flow rates and concentrations of influent were conducted for various other parameters such as hardness, sulphate, nitrate, chloride and iron. The removal of iron was always above 95% and there was no change in its removal efficiency with increase in filtration rates and concentrations.

Nehrenheim *et al*. (2008) propose field studies for treating landfill leachate, which depends on various metal concentrations and other environmental factors. As the residence time is increased, the ion retention rate is also increased. The removal of heavy metals from landfill leachate depends on pH and chemical composition of the media and the characteristics of leachate water (Kietlińska and Renman 2005). The removal efficiency obtained was 66% for copper and 62% for zinc. A significant reduction could not be achieved for other metals except nickel (19%) and molybdenum (16%). Koupai *et al*. (2015) demonstrated its application in urban stormwater treatment along with porous concrete in the presence of sand filter and found 44% reduction in COD and more than 90% reduction for both total suspended solids and lead.

A hybrid wetland system used by Saeed *et al*. (2012) for treating tannery wastewater was similar to the one carried out by Korkusuz *et al*. (2007) for domestic wastewater. The horizontal flow wetland system used cupola slag and removed an average phosphate of 61% by adsorption alone. Korkusuz *et al*. (2004) previously suggested that constructed wetlands would be successfully employed for secondary and tertiary treatment of wastewater in Turkey. The average removal efficiencies for total suspended solids, chemical oxygen demand, ammonia nitrogen, total nitrogen, phosphate-phosphorus and total phosphorus were 63%, 47%, 88%, 44%, 44% and 45% respectively (Korkusuz *et al*. 2005). A later study by Ge *et al*. (2014) on remediation of highly polluted river water using horizontal subsurface flow constructed wetland systems using slag and gravel media was effective for *Phragmites australis* growth. The dissolved metals could be removed considerably by uptake of plants or by wetland treatment (Hallberg and Renman 2008). The polluted river water was fed intermittently for the favourable condition for plant growth and development of biofilm. Higher coefficients of correlation could be achieved when fitted to Langmuir isotherm equation for slag than gravel. Adsorption for slag was 3.15 mg/g whereas gravel recorded only 0.81 mg/g (Ge *et al*. 2015). Surface adsorption and diffusion into the slag brought about the phosphorus adsorption. It might also be due to higher content of calcium in slag, as supported by Johansson and Gustafsson (2000) and Korkusuz *et al*. (2007). The average removal efficiencies of COD and BOD_5 using slag were 72.4% and 84.3% respectively when compared with gravel. The Total-P in wastewater consisted of 47.3% suspended and 57.3% dissolved parts of which 70.6% removal of suspended Total-P could be achieved. Nitrogen removal was also reported during the study period of 2 years. But the findings indicated that the plants grown in slag could absorb fewer nutrients compared to gravel media. It could be further extended on a large scale. Although particle size and texture of slag could result in better growth of plants, leaching of chemicals from slag, especially the release of phytotoxins such as zinc and the presence of less organic matter might have created stunted growth of eelgrass (Hizon-Fradejas *et al*. 2009). There was a possibility of producing leachate with high pH values and electrical conductivities when steel slag was used in constructed wetlands. In order to counteract these problems, effective pre-treatment methods are to be implemented before its utilization (Hizon-Fradejas *et al*. 2009, Blanco *et al*. 2016).

The main operational problem of any filter is clogging due to excessive organic loading which reduces the filter efficiency. The risk of clogging in wastewater treatment due to organic solids was reported by Hedstrom and Rastas (2006) and Westholm (2010). The mechanical adsorption also increased the head loss resulting in clogging of the media as pointed out by El-Taweel and Ali (2000). A remedial measure such as pre-treatment to remove total suspended solids from wastewater has been suggested by Hallberg and Renman (2008).

5. Conclusions

The applications of slag are manifold in water and wastewater treatment. The essential characteristics find its use as a filter media and thus, it is an excellent alternative source for replacing sand.

- Even though the lab-scale and field trials show positive results, its implementation on a large scale needs to be studied.
- The adsorption and chemical precipitation may sometimes encounter physical clogging.
- The recovery or regeneration technologies are found to be effective only for a small duration.
- Innovative researches are being done in constructed wetlands using slag as media but its longevity is to be determined.
- Since the slag is disposed of in large quantities around the premises of ferrous industries, its effective utilization in pollution remediation technology should be strongly appreciated.
- The literature strongly recommends the need for developing an appropriate technology for reusing ferrous slag in water/wastewater treatment which would be effectively, efficiently and environmentally managed for a long duration.

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