Biosorption of Heavy Metals in Industrial Effluents: A Review

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Abstract

Industrial processes consume large quantity of water and produce highly polluted effluents containing recalcitrant contaminants which are found to be toxic even at trace concentrations. Adsorption was reported to be effective in the removal of heavy metal ions in a solution of varied toxicity. Despite this credit, however, adsorption was faced with some setbacks ranging from adsorbent cost, incomplete removal of pollutants, and production of large volume of sludge. Microorganisms, especially microalgae play vital roles in the adsorption of metal ions due to the anionic ligands in their cell walls which attract metal cations in solution, provide best removal efficiencies by their ability to reproduce in short time, remove micropollutants at minute concentrations as well as serve as feedstock for renewable energy alternatives, after wastewater treatment.

Keywords: adsorption; biosorption; heavy metals; ligands; microalgae; toxicity

INTRODUCTION

Anthropogenic activities including industrial production, rapid increase in population, agricultural activities and urbanization have led to enormous pollution (Abdel-raouf *et al.*, 2012; Agarwal *et al.*, 2019; Aljaberi and Mohammed, 2018), due to the generation of waste containing toxic and persistent pollutants such as heavy metals (Akan *et al.*, 2007; Bilal *et al.*, 2018; Biswas *et al.*, 2018), nutrients (Jia and Yuan, 2017), inorganic and organic substances (Abdel-raouf *et al.*, 2012) and greenhouse gases (GHGs) (García *et al.*, 2017) and its subsequent discharge into the water course untreated or partially treated (Akan *et al.*, 2007; Arumugam *et al.*, 2018; Iqbal *et al.*, 2019) as traditionally known location of industrial facilities are situated near streams and/or river to discharge their huge polluted effluents to the bodies of water (Desta *et al.*, 2017), which has detrimental impacts to the lives and natural ecosystems.

Significant concentrations of metal ions, inorganic substances and organic matter have been identified in agricultural, industrial and municipal wastewater (Agarwal *et al.*, 2019; Ballén-segura *et al.*, 2016), in which majority of these effluents from industries were non-biodegradable of varying degree of toxicity as pesticides, nutrients and heavy metals and other emerging contaminants (Aljaberi and Mohammed, 2018; Bilal *et al.*, 2018), due to their high mobility and solubility, toxicity and tendency to migrate and accumulate along the food chain (Bulgariu & Bulgariu, 2014; Burakov *et al.*, 2018). These pollutants are of great concerns with respect to their serious environmental and health problems.

Among the industries, tanneries were identified as pollution-intensive due to production of effluents with complexes of high strength and varied wastewater characteristics (Mahmoud & Mohamed, 2017). Leather production utilizes high amount of water ranging from 34 to 56 m^3 per ton of hide (Lofrano *et al.*, 2013), generates about 80% solid waste and wastewater (Desta *et al.,* 2017; Mekonnen, 2006; Wang *et al.,* 2016). This differs based on the size and magnitude of tanning, the raw materials, method of tanning and targeted finished products. About 90% of the leather produced worldwide is through chrome tanning (Belay, 2010) and only 50-70% of chromium (Cr) salts used are absorbed in to the process (Islam *et al.,* 2014).

The global environmental challenges in the leather production are the treatment and safe disposal of effluents containing Cr in high concentrations having mutagenic, carcinogenic and teratogenic properties (Mahmoud and Mohamed, 2017; Durai and Rajasimman, 2011; Wang *et al.,* 2016) especially the most toxic hexavalent chromium which was found to be about 100 times more toxic than trivalent chromium and is capable of inhibiting biological activities (Vendruscolo *et al.,* 2016) and are the most stable Cr oxidation states (Wang *et al.,* 2016; Sibi, 2016). Cr (III) is more stable and important for metabolism in small quantities, as triglyceride, cholesterol and is essential for maintaining glucose levels and other nutritional importance (Vendruscolo *et al.,* 2016).

Effluents from tanning process usually consist of high values of toxic heavy metals such as chromium (Cr), copper (Cu), nickel (Ni), zinc (Zn), iron (Fe), cadmium (Cd) and lead (Pb), especially Cr(VI) with its carcinogenic property (Ajayan *et al.,* 2015; Dai *et al.,* 2012; Mahmoud & Mohamed, 2017) to damage haploid set of chromosomes, teratogenic (Arumugam *et al.,* 2018; Lage *et al.,* 2018) capable of disrupting the development of embryo and foetus and can also halt pregnancy or can lead to congenital malformation in birth, and mutagenic as capable of changing genetic make-up, thus increasing the frequency of mutation above natural background level thereby affecting quality of life and the environment (Goswami & Mazumder, 2013; Igiri *et al.,* 2018; Jobby *et al.,* 2018) It can also damage internal organs such as liver, kidney, pulmonary system and skin even at lower concentration (Bilal *et al.,* 2018).

Heavy metals were characterized as extremely positively charged cations, with an atomic weight of more than 55.8 g/mol of Fe and/or a specific gravity higher than 5.0 and their ions are poisonous and toxic even at minute concentration (Aljaberi and Mohammed, 2018). Due to the toxicity, non-biodegradability and bioaccumulation of heavy metals (Igiri *et al.,* 2018) that are produced as a result of industrial processes such as tanning, electroplating, metal finishes, textile, mining, glass, ceramics, storage batteries, dying, paper and pesticide production (Fu and Wang, 2011; Godwin *et al.,* 2019) and the rate at which such recalcitrant pollutants were produced and their detrimental effects to the lives and environment coupled with persistent nature especially in aqueous solution and food chain (Burakov *et al.,* 2018), there is need for efficient, cost effective, renewable, environmental friendly and sustainable industrial wastewater treatment approach (Biswas *et al.,* 2018; Mohammed, *et al.,* 2014a) that will be guarantee continuous industrial production and effluents meet the ever increasing stringent discharge regulations.

In view of the problems associated with Cr tanned wastewater, there is a growing concern of increasing environmental degradation due to the persistent nature and higher solubility of Cr (VI). Several studies were conducted in order to treat tannery effluents using physico-chemical treatment approaches including adsorption (Louarrat *et al.,* 2017), chemical precipitation (Wang *et al.,* 2016a), ion exchange, solvent extraction, coagulation and filtration (Akhondi *et al.,* 2017; Chowdhury *et al.,* 2013), electrochemical treatment (Sarala *et al.,* 2012), membrane technology (Fettig *et al.,* 2017) and reverse osmosis were employed in order to treat industrial effluents (Godwin *et al.,* 2019).

Adsorption as Remediation Tool

Adsorption is widely employed as a tool for industrial effluent treatment as appeared to have huge influence on heavy metals transportation, bioavailability and toxicity (Burakov *et al.,* 2018) and as such was found to be effective in the removal substantial amount of metal ions in the wastewater. As described by Gadd, (2009), adsorption involves substance incorporation from one state of matter to other as adhesion physically or ions bonding of adsorbate to the adsorbent. Functional groups including hydroxyl, carboxyl, sulfhydryl and many more with negatively charged surfaces (Ballester *et al.,* 2007; Surayya *et al.,* 2019) were present for majority of the solids including microorganisms that promote the adsorption of the highly positively charged metal ions to their surfaces from the solutions.

Activated carbon (AC) adsorbents were extensively employed for the metal ion remediation, due to large surface area and high microspores and were found to be effective. Louarrat *et al.,* (2017) reported a high Cr removal efficiency that ranges between 73-78%, when AC from leather shaving and goat hair after activation physically. Another research indicated a range of sorption capability of AC prepared from Nigerian Bamboo tree in order of $Cd^{2+} > Zn^{2+} > Pb^{2+} > Ni^{2+} > Cu^{2+} > Cr^{3+}$ (Taiwo & Chinyere, 2016). In a related development, (Chen *et al.,* 2018), explore the use of wood-based powdered activated carbon in Cr(VI) removal and establishes that the highest Cr(VI) removal was 40.04% at pH of 3.0, while higher pH of 10.0 the removal efficiency decrease to as low as 0.34%.

In these days, the continuous depleting of conventional coal-based AC sources with its subsequent rise in price coupled with intensive energy requirement for steam up to 1100^0C (Fu and Wang, 2011; Pradeep *et al.,* 2016) and associated emissions in the production process. This has called for a renewed quest for an alternative adsorbent with more adsorption capabilities and can be obtained freely from environment. In order to improve the adsorption of metal ions by AC, introduction of composites and additives could serve as an alternative and may include the use of surfactants, tannin acids, magnesium (Fu and Wang, 2011) and alginate (Mahmoud and Mohamed, 2017).

In addition to this, a composite material known as biochar was produces in air-restricted situation to obtain a carbon-rich, porous and fine-grained material from organic matter degradation. Its production at excessive temperature of about 700^0C led to the biochar with few O_2 and H functional groups with carbon layer well organised. Otherwise, at about 4000C a biochar with variety of characters as cellulose and aliphatic type structures and a more C=C and C-H functional groups was produces (Godwin *et al.,* 2019) in order to enhance the adsorption capacity of the pollutants.

Moreover, in an earlier submission, Rangasamy *et al.,* (2014) employed the use of zeolite in the adsorption process and ascertained that, the adsorption of Cr(VI) ions increases by increasing the concentration of zeolite and at 100µg/g of zeolite, about 80µg/g of Cr(VI) was adsorbed from dichromate solution. Apart from these several physico-chemical treatment approaches were conducted by numerous researchers in order to optimised heavy metal removal efficiencies from industrial effluents remediation and Fig 1 summarized some of these treatment technologies.

Table1: Prospects of Activated Carbon (AC) Adsorption

S/N	Treatment Approach	Major Findings	References

1	Adsorption using leather shaving (LS) and goat hair (GH) AC	decrease in chromium concentration by 78% and 73% for the activated carbon prepared from (LS) and (GH), respectively	Louarrat *et al.*, (2017)
2	Production of AC from Nigerian bamboo tree and subsequent heavy metal removal	Removal efficiency in order of $Cd^{2+} > Zn^{2+} > Pb^{2+} > Ni^{2+} > Cu^{2+} > Cr^{3+}$	Taiwo and Chinyere, (2016)
3	Production of AC from granulated shell	The external surfaces of the chemically activated carbon is full of cavities, but associated with excessive use of chemicals for impregnation and energy up to 1000 ^{o}C for carbonization	Aji *et al.*, (2015)
4	Wood-based powdered activated carbon for Cr(VI) removal	highest Cr(VI) removal was 40% at pH 3, while higher pH of 10.0 led to decrease in removal efficiency to as low as 0.34%	Chen *et al.*, (2018)
5	Baker's yeast isolates pre-treated with calcium alginate	Decrease in Cr(VI) ions up to 85%	Mahmoud and Mohamed, (2017)
6	100 µg/g of zeolite in Cr(VI) removal	About 80 µg/g of Cr(VI) was adsorbed from dichromate solution	Rangasamy *et al.*, (2014)
7	Settling, filtration using sand-stone and saw-dust and then coagulation ($FeCl_3$) from 50-500 mgL^{-1}	150 mgL^{-1} coagulant dose with a pH near neutral provide highest treatment efficiency though with high TDS above 4000 mgL^{-1}	Chowdhury *et al.*, (2013)
8	Synthesis of 2-hydroxylethyl-tri-methyl ammonium chloride (HGCTS) for Cr(VI) adsorption	Max adsorption capacity was 250 mgL^{-1} and the detection limit was 20 mgL^{-1}	Dai *et al.*, (2012)
9	Cr(VI) adsorption using formaldehyde treated saw-dust and charcoal of sugarcane bagasse at ratio of 1:4 (Saw-dust : Formaldehyde)	Removal of Cr(VI) was found to increase with initial increase in concentration	Dhungana & Yadav, (2009)
10	Adsorption of Cr(VI) using calcium phosphate	Maximum adsorption attained within pH range of 1 to 5	Elyahyaoui *et al.*, (2017)
11	Tannery effluent treatment by sedimentation, dissolved air floatation, membrane bioreactors (MBR) and then polishing using granular activated carbon	Up to 81% removal efficiency by MBR for organic substances and total nitrogen removal of 36% was recorded	Fettig *et al.*, (2017)
12	Domestic wastewater treatment in an intermittent aeration reactor followed by dissolved-air floatation	Removal efficiency of: COD = 92%, P = 90%, PO_4^{3-}= 84% for raw samples and 94% for filtered samples	Marchetto, (2013)

13	Alkalis precipitation and Cr speciation	Cr concentration > 5000 mgL^{-1} reduced to about 20 mgL^{-1} with Cr(III) complexation	Wang *et al.*, (2016)

Setbacks Associated with Adsorption methods

Based on this, physico-chemical treatment methods mostly were found to be faster (Goswami and Mazumder, 2013) and accommodate extremely higher metal ions up to 5000 mgL^{-1} as reported by Wang *et al.*, (2016), but, however, produced high amount of sludge, high energy demand, costly due to chemical employed and inability to remove multiple pollutants as well as remediation of contaminants at concentrations below 20 mgL^{-1} (Dai *et al.*, 2012; Wang *et al.*, 2016) which is much higher than discharge limit of Cr of 0.5 mg/L by National Environmental Standards and Regulations Enforcement Agency (NESREA) (Akharame and Olurunfemi, 2017), and if left untreated may affect quality of lives and the environment. Bwapwa *et al.*, (2017) also reported that microalgae are efficient in removing low concentration of contaminants especial in aqueous medium.

The ever-increasing cost of chemicals, inefficiency, incomplete removal, enormous sludge production and excessive energy requirements make physico-chemical treatment unattractive (Burakov *et al.*, 2018). As reported by Jia and Yuan, (2017), mechanical aeration used in providing large quantity of air or oxygen accounts for about 45-75% of the total energy cost required for the running of the plants (Anbalagan *et al.*, 2016;Marazzi *et al.*, 2019). In addition, waste sludge produced almost equals the quantity of treated wastewater as pointed out by Metcalf and Eddy, (2003) amounting to 70-100 kg of dry activated sludge while treating 1ML of wastewater. This increases as the treatment continues, coupled with excessive demand in area of land and energy to treat the produced waste activated sludge (Jia & Yuan, 2017).

On the other hand, several researches were carried out in order to develop a cost effective, productive, efficient, environment-friendly and sustainable adsorbent that can remove pollutants, maintain natural balance and treat wastewater. In line with this, microorganisms such as fungi (Abatenh *et al.*, 2017; Irobekhian *et al.*, 2017), bacteria (Sole-bundo *et al.*, 2018; Solé-bundó *et al.*, 2019) and microalgae (Mohammed, 2013; Mohammed et al., 2014a; Zhu et al., 2014, 2018) were found to be promising options as they can grow in the wastewater, assimilate nutrients to mitigate eutrophication (Cai *et al.*, 2013; García *et al.*, 2017), adsorb metal ion due to their cell characteristics (Bilal *et al.*, 2018; Jobby *et al.*, 2018; Shalaby *et al.*, 2019; Wang *et al.*, 2016b) and do not emit gases such as CO_2 which contribute to global warming (Pathak *et al.*, 2019) as compared to conventional wastewater treatment systems.

Bioremediation

Extensive distribution of microorganisms and their adaptation on earth, simple nutrition and metabolism can be utilized in contaminants biodegradation (Abatenh *et al.*, 2017) which is referred to bioremediation process. This was considered successful process due the capacity of some microorganisms to utilize pollutants as nutrients for biomass production (Sun *et al.*, 2019), biotransform toxic heavy metals to nontoxic or less toxic as in conversation of Cr(VI) to less toxic Cr(III) within their cells (Jobby *et al.*, 2018). In addition, these organisms also provide renewable energy alternatives ranging from biofuels (Marazzi *et al.*, 2019), biodiesel (Pathak *et al.*, 2019), biomethane (Milledge *et al.*, 2019), and many other valuable compounds such as pigments (Agarwal *et al.*, 2019) that are used in the manufacture of personal care products and pharmaceuticals (Mohammed, 2013; Whitton *et al.*, 2015).

Among these microorganisms, microalgae have proven to be versatile due to their ability to grow in wastewater (Fernández-linares *et al.*, 2017; Hammouda *et al.*, 2015), photosynthesize their own food by utilization of energy from sunlight (Agarwal *et al.*, 2019) and surrounding CO_2 (Brennan and Owende, 2010; Cabello *et al.*, 2017), assimilate nutrients to reproduce (Hammouda *et al.*, 2015; Sakthivel and Elumalai , 2016; Wang *et al.*, 2016c) and absorb, accumulate, transform and degrade pollutants (Bhatnagar & Sillanpää, 2010; Biswas *et al*., 2018; Jobby *et al*., 2018) as they possess cell walls containing functional groups (Utomo *et al.*, 2016) consisting of anionic ligands (Igiri *et al.*, 2018; Vendruscolo *et al.*, 2016) of polysaccharides, proteins, lipids (Zhu *et al.*, 2014) which can attract positively charged metal ions and accumulate contaminants (Burakov *et al.*, 2018) through their cytoplasm (Hammouda *et al.*, 2015) especially using vacuole (Perpetuo *et al.*, 2011). Algae been O_2 evolving organisms can help in oxygenation and mineralization of organic matter (Ajayan *et al.*, 2015).

Prospects of Microalgae Wastewater Treatment

Microalgal wastewater treatment systems coupled with carbon capture can potentially reduce greenhouse gas emission (Mohammed *et al*., 2014a; Morales *et al.*, 2017), consume less energy, provide renewable energy alternatives, remove pollutants from wastewater, adsorb and/or absorb heavy metals, degrade organic matter (through the use of organic carbon by heterotrophic microalgae) with subsequent nutrient utilization (García *et al.*, 2017; Su *et al.*, 2017). They also provide another opportunity for nutrient recovery with consequent climate change and eutrophication mitigations. Microalgae can play a role in industrial effluent treatment including their potential to grow wastewater, capture carbon and recover phosphorus and nitrogen. This approach is fast growing treatment due to its sustainable and eco-friendly nature. One of the unmatched excellences of microalgae is their size, regular supplement of nutrients and optimum physiological condition to grow and multiply their cells within short period of time (Mahmoud and Mohamed, 2017; Mekonnen, 2006).

Algae have much higher rate of photosynthesis than terrestrial plants (Agarwal *et al.*, 2019) as such have extremely higher growth rate which was estimated to be around 70 $MTha^{-1}yr^{-1}$ in specific reactors than about 3 $MTha^{-1}yr^{-1}$, 9 $MTha^{-1}yr^{-1}$ and 10-13 $MTha^{-1}yr^{-1}$ for soya beans, corn and hybrid poplar or switch grass, respectively (Abdel-raouf *et al.*, 2012). Mohammed *et al.*, (2014) reported a highest biomass productivity and growth rate of 0.034 $gL^{-1}d^{-1}$ and 0.109 d^{-1} at intermediate irradiance of about 580 $\mu mol/m^2s$ in hybrid microalgae-activated sludge system. In a similar development, Lage *et al.*, (2018) reported that in a mixotrophic growth, the presence of inorganic and organic carbon lead to high growth rate and biomass production. After 17 days of cultivation, Benítez *et al.*, (2018) obtained biomass growth rates of 9.8 x 10^3 and 4 x 10^2 cells/mL with corresponding biomass production of 1.8 and 0.6 mg/L with agitation and aeration, respectively. This was attained at temperature ranging from 21.5 to 25.3 ^oC with illumination of about 422 $\mu mol/m^2s$ in 10 L photobioreactors (PBRs).

Symbiotic relationship exist between algae and bacteria in wastewater treatment (Chen *et al.*, 2019) in which bacteria consume oxygen (O_2) as a by-product of microalgal photosynthesis to degrade waste substances with aeration from O_2 produced (Anbalagan *et al.*, 2016; Marazzi *et al.*, 2019) and consequent production of carbon dioxide (CO_2) which is required by microalgae in the presence of light (Mohammed, 2013) and moisture from wastewater to photosynthesize and grow with subsequent gas exchange and purification of wastewater.

In light reaction, photosynthetic pigments extract energy from alternative illumination provided by red light-emitting diodes (LEDs; Mohammed *et al.*, 2014b) which is converted to chemical energy, by producing high energy molecules known as adenosine triphosphate (ATP) and nicotinamide adenide dinucleotide phosphate (NADP), while the products of dark reactions are formed in the production phase and include carbohydrates, amino, fatty and organic acids (Appelberg, 2013).

Several algae species were used in the bioremediation of nutrients, heavy metals, pathogens and many other pollutants (Ardila *et al.,* 2017; Bilal *et al.,* 2018; Subashini and Rajiv, 2018). Microalgae show the ability to absorb/adsorb inorganic pollutants in to their cell components. Negatively charged organic ligands (hydroxyl, carbonyl, phosphoryl and sulfhydryl groups) contributed enormously to the bioremediation process by attraction and attachment with other atoms (Bilal *et al.,* 2018; Ozturk, *et al.,* 1999). The most dominant algal species employed in wastewater treatment include the genus Scenedesmus and Chlorella which were found to have high degree of tolerance. These unicellular organisms protected by rigid walls are fast growing and efficient in removing nutrients from various wastewater sources (Delrue *et al.,* 2016). Their higher degree of stability in water medium and being smaller in size, however, is the major setback associated with single strain microalgae especially in the recovery of the algae after treatment.

Microalgal culture consisting of particular specie isolated to obtain a required or targeted parameter with maximum yield. Freely cultivated microalgae in open cultures are likely to be taken over by past growing aggressive species unless supplementary steps are taken to control the media for longer time. Mixed culture of algal species was observed to be more stable and the changes between different species influence growth and biomass production. Mixed culture system can be more adaptive to environmental conditions, while the conditions may not be favourable to a specific axenic culture. In mixed culture systems, other microalgae species may be more adapted to new media conditions and grow dominant (Lage *et al.,* 2018). Complex microbial consortia have also been shown to be better adapted to handling and degrading toxins and creating a more stable waste management (Krustok, 2016). Komolafe *et al.,* (2013) compared two mixed culture wastewater in (PBRs) to a system inoculated with only *Desmodesmus sp.* while it is showing a higher maximum biomass concentration of 0.58 gL^{-1} compared to 0.45 gL^{-1} of a mixed culture dominated by *Oscillatoria* and *Anthrospira* having a higher lipid, fatty acid and methyl esters yield.

Owing to reliance on light energy by photosynthetic algae, its availability and receptibility is important. Increase in biomass production depends on optimized light use efficiency as well as nutrient uptake from wastewater. Mohammed, (2013) developed a hybrid microalgal system for municipal wastewater treatment with characteristic red wavelength of 660 nm and argued that growth and production of algae were always not correlated to irradiance in a batch PBR system and also reported that intermediate value of irradiance of about 580 $\mu mol.s^{-1}.m^{-2}$ using red LEDs to treat domestic wastewater at about 4 d hydraulic retention time (HRT) and 300 mgL^{-1} biomass concentration was found to be optimal for operating the PBRs.

This optimum irradiance is within the photosynthetic active radiation (PAR), due to the fact that most familiar *chlorophyll-a*-containing organisms cannot use light longer than 700 nm. Red LED wavelengths are beneficial for microalgal biomass production and effective in influencing photosynthesis as they are poorly absorbed by water molecules (Mohammed *et al.,* 2014b). LED has the potential in replacing the traditional light sources for microalgal cultivation due to the advantages of the LED which include low power consumption, luminous efficiency, quick start, easily checked, monochromatic emission and elongated useful time (10) up to ten years (García *et al.,* 2017; Mohammed et al., 2014b; Whitton et al., 2015).

HRT was found to be among the essential factors which can influence microalgal productivity and also affect microalgal wastewater treatment efficiency (Larsdotter, 2006). Some researches indicated that 4day HRT was essential for efficient removal of pollutants and nutrients in photobioreactors (Larsdotter, 2006; Mohammed *et al.,* 2014a), at low and moderate concentrations of wastewater. It was also indicated that longer HRT may be outranked in obtaining sufficient treatment of pollutants. Moreover, higher HRT increases the significance of the treatment. On the other hand, solid retention time (SRT) being average time the activated sludge solids are in the system, SRT is an important design and operating parameter for the activated sludge process (Anbalagan *et al.*, 2016; Luo, *et al.*, 2016). Too low SRT signifies incomplete denitrification, elevated N in treated effluent and higher chemical usage in denitrification filters, while too high SRT increased oxygen requirements and energy usage (Smith *et al.,* 2013) and so, a moderate SRT may be more suitable in order to avoid the two extreme conditions.

Several abiotic factors such as light, pH, CO_2, nutrients, temperature, O_2, salinity, and biotic factors as species competition, operational conditions such as depth, mixing, dilution rate, inhibiting substances and frequency of harvesting, play detrimental role in the success of microalgal wastewater treatment. Among these, light, pH, nutrients, CO_2 and mixing were found to be of utmost importance (Demirel *et al.*, 2018) and were discussed.

Light

In a quest to increase the algal growth in the PBRs, requirement for light is paramount due to its role in photosynthesis as such should be provided appropriately in relation to wavelength, duration and intensity (Al-hadabi *et al.,* 2012). It was accepted that plants and related photosynthetic organisms utilizes at photosynthetically active radiation at a range between 400-700nm wavelengths (Mohammed, 2013; Mohammed *et al.*, 2014b). Different light sources were employed to illuminate the algal cultures, which range from the use of fluorescent tube to the light emitting diodes (LEDs) of varying colour and intensity. Among them, red LEDs were found to be efficient within the absorption spectrum of the photosynthetic pigments, weakly absorbed by water molecules, economical as well as efficient (Al-hadabi *et al.,* 2012; Mohammed *et al.,* 2014b).

Optimum irradiance should be provided in order to achieve a higher growth rates and biomass productivity that determines the success of the treatment approach. Excessive illumination may cause photoinhibition while low intensity provision may lead to light limitation with subsequent retardation of growth. Al-hadabi *et al.*, (2012) reported that light increase between 37.5-62.5 $\mu molm^{-2}s^{-1}$ brings about an increase in biomass whereas at about 100 $\mu molm^{-2}s^{-1}$ biomass decrease and as such suggested a range between 14.7-55.5 $\mu molm^{-2}s^{-1}$ for small size PBRs. Findings from Mohammed *et al.,* (2014b) show that the biomass growth and productivity are not always directly proportional to irradiance as the highest was obtained at intermediate irradiance of 582.7 $\mu molm^{-2}s^{-1}$. However, influence of different light intensities on some parameters other than biomass growth and productivity should be investigated as such to understand how irradiance may influence the production of valuable algal extracts such as biofuels, biodiesel, lipids, pigments etc.

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pH

pH is one of the essential parameter that dictate the nature and distribution of charges of the functional groups surfaces of the adsorbent to that of the cation in solution (Abas *et al.,* 2013). It also has high effect on algal metabolic activities with greater impact on biochemical proportion of the effluent and also influences the solubility of O_2, CO_2 and mineral salts in the solution. The reduction of ammonia, phosphates, BOD, disinfection and other metals may be resulted by elevated pH values (Agarwal *et al.,* 2019). Huge variations with regard to pH may affect the biomass growth.

Alteration of pH levels has tremendous effects on the biomass growth, availability of CO_2 and Carbon, as well as nutrients and trace metals (Pathak *et al.,* 2019). Physiological processes of both marine and freshwater microalgae, was affected by elevated pH level which found to distract the structural lipid and subsequent reduction of its content in some species of organisms. In this development, pH also influences the chemistry of metal ions solution, activity of the biosorbent surfaces and contest among the heavy metals ions in the medium (Perpetuo *et al.,* 2011).

Nutrients

High concentration of nutrients in wastewater such as nitrogen (N) and phosphorus (P) may results in eutrophication in seas, oceans and lakes which has tremendous impact to aquatic life and ecosystem (Benítez *et al.,* 2018). One of the requirements for wastewater treatment system is the heavy metal ions and nutrients (mostly N and P) removal (Mohammed, 2013) that will conform to ever increasing discharge regulations. N was among the essential requirements needed to support the growth at all level in the living organisms and exists in various substances including enzymes, proteins, peptides, chlorophyll and other cell contents, usually in the form of N_2, NO_2^-, NO_3^- and NH_4^-. Algae engaged in the transformation in to organic N from inorganic form through assimilation and sometimes fixation as in the case of atmospheric N (Cai *et al.,* 2013).

The biotreatment of effluent with microalgae to remediate nutrients as N_2 and P with consequent O_2 production for bacterial degradation was started more than 60 years ago by (Oswald and Gotaas, 1955). Since then, several researchers conducted series of laboratory and pilot studies for sewage and other industrial effluents treatment by this approach (Mohammed, 2013). N_2 in wastewater comes from metabolism while about 50% of P comes from synthetic detergents. The main structures in which they exist in effluent include NH_4^+, NO_2, NO_3 and PO_4^{3-} (Benítez *et al.,* 2018). These are the main forms of nutrient and their stripping is nutrient removal and failure to remove nutrients in the effluent leads to eutrophication and subsequent environmental degradation (Mohammed, 2013).

The most preferred form of inorganic N by all eukaryotes for assimilation is NH_4^-, NO_2^- and NO_3^-. This transformation occurs in the membrane and then reduction of NO_2^- and NO_3^- in their oxidized form with the help of nitrite and nitrate reductases (Singh & Singh, 2014). Nicotimide adenine di nucleotide (NADH) in its reduced form was used by NO_3^- reductase to give out 2 electrons resulting to NO_2^- transformation. NO_2^- was further reduced to NH_4^- by NO_2^- reductase and which ferredoxin transferring 6 electrons. All these sources of inorganic N were virtually reduced to ammonium which incorporated in to amino acids in the cell contents. Lastly, glutamate, glutamine synthase and ATP contrasted the incorporation of NH_4^- to amino acid (Benítez *et al.,* 2018).

Researches indicated that the microalgae prefer NH_4^- than NO_2^- and NO_3^- and their assimilation occurs when almost NH_4^- was utilized (Luo *et al.,* 2016). As such, effluent or in general wastewater with elevated levels of NH_4^- can be efficiently employed in rapidly growing algae. Though microalgae prefer NH_4^- but NO_3^- been more oxidized form and most stable thermodynamically in aquatic medium and thus predominant. Ammonium tolerance for species of algae ranges from 25-1000µmol NH_4^--NL^{-1} (Cai *et al.,* 2013). Scenedesmus was found to grow well in anaerobic digestion effluent at ammonia concentrations of up to 100 mgL^{-1}; however, increasing ammonia concentration to 200–500 mgL^{-1} led to a decrease of biomass by up to 70% (Luo *et al.,* 2016). Metabolic activities of the cell was not only the mechanism for ammonium removal but rather ammonium reduced through stripping, where at elevated pH and temperature large quantity of ammonia can easily volatized.

On the other hand, P is vital in algal metabolic activities and located always in lipids, nucleic acids, protein and intermediate cell transformation carbohydrate. The combination of inorganic P in to organic substances in the algal cell by phosphorylation that lead to the production of ATP from adenosine di phosphate (ADP) followed by energy formation (Cai *et al.,* 2013). Algal cells usually used phosphorus in the manufacture of adenosine triphosphate (ATP), nucleic acids and phospholipids (Ballén-segura *et al.,* 2016; Hammouda *et al.,* 2015) was assimilated as preferably soluble orthophosphates such as HPO_4^{2-} or $H_2PO_4^-$ (Ballén-segura *et al.,* 2016; Mohammed and Mota, 2018) and also algae generated as a result of photosynthesis that induces change in pH that may enhances N and phosphates precipitation
About 90% of ammonium removal efficiency was attained when a hybrid microalgal-activated sludge treatment system developed by Mohammed, (2013), was used to treat a synthetic municipal wastewater at a hydraulic retention time (HRT) of about 4days, with optimum irradiance of 582.7µmol/m^2s with efficient stirring of 100±rpm. In related research to also treat domestic wastewater with CO_2 enhancement by García *et al.,* (2017), an increasing the efficiency of the removal was recorded from 38-81%, 39-97% and 59-64% for total nitrogen, ammonium and phosphates respectively. The CO_2 addition support almost compete nitrification of ammonium to nitrate. Capability of *Scenedesmus sp.* in the nutrient remediation was reported by Ballén-segura *et al.,* (2016) with efficiency of 90 and 99% removal of inorganic nutrients as NO_3 and PO_4^{3-}, respectively, and that the production of adenosine triphosphates (ATP), phospholipids and nucleic acids essential for cellular metabolism were produced in the cell by phosphates. Also algae derived as a result of photosynthesis initiate change of pH that increases the precipitation of nutrients especially P and N.

Benítez *et al.,* (2018) reported a removal of N and P using a local microalgal strain with consideration of the effect of agitation and aeration. The result shows that in the PBR for agitation and aeration, the NH_4^--N and PO_4^{3-}-P removal efficiencies were 52.6 and 55.6% and 67.0 and 20.4%, respectively. The NO_3^- production efficiencies reaches 87.0 and 93.1% for agitation and aeration PBRs respectively and this supported the submission that nitrates was more oxidized, most stable and predominant in aqueous medium. Despite this advancement in nutrients bioremediation, little attention was paid in the recovery of the huge quantity of nutrients been absorbed by the adsorbents and if not recovered there is high tendency of recycling pollution back to the environment.

CO_2 Assimilation

Combustion of fuels, industrial productions and conventional wastewater treatment systems were identified as significant CO_2 emission sources which in turn pollute the air and atmosphere in general as being among the greenhouse gases (GHGs). In order to mitigate the impact of CO_2 emission, a green, economical and sustainable remediation process is needed with less or no energy requirement, zero emission and do not produce waste sludge which its treatment will escalate the process cost.

Algae were found to be the best option, as it utilizes the CO_2 present with the help of solar energy or any artificial alternative source to photosynthesized, grow and produce biomass with numerous applications and then emit only O_2 which is one of the valuable substance needed by each quarter. In addition to that, microalgae were known to fixate CO_2 from atmosphere (Cabello *et al.,* 2017), or other more concentrated sources for consequent biomass growth (Ketife *et al.,* 2017).

Highest algal growth will be achieved when efficient transfer of CO_2 from gas to liquid phase, liquid oxygen to gaseous phase, mixing, light distribution, photosynthesis, cell growth and initial conditions of operation which include biomass concentration, pH, irradiance, gaseous CO_2 content and nutrients requires much closely monitoring and control to obtain maximum performance. Algae convert soluble CO_2 to cell contents such as carbohydrates, lipids, nucleic acid and proteins and the availability of the liquid CO_2 with the dependence on amount and mass transfer rate from gas to the liquid, strongly influence the productivity of the biomass (Cabello *et al.,* 2017).

Majority of microalgae survives in low amount of CO_2 and exhibit growth at CO_2 levels (Cabello *et al.,* 2017) and a single specie biomass CO_2 rate of fixation may vary and the variation will be in the range of $0.5\text{-}1.2g_{co2}g_b^{-1}d^{-1}$. A specific amount will be dependent upon the light intensity, amount of CO_2 and HRT, and for *B. braunii* shows some lower rates but a higher maximum microalgal biomass concentration. Results for *C. vulgaris* and *S. obliquus* shows median fixation rate of CO_2 between 0.09-0.35 and $0.098\text{-}0.26g_{co2}g_b^{-1}d^{-1}$ respectively (Ketife *et al.,* 2017). The rate of consumption of *Scenedesmus* was analysed at various time. The maximum apparent CO_2 rate of consumption at $336\mu molm^{-2}s^{-1}$ and 5.6% of CO_2 was $6530mg_{co2}g_b^{-1}d^{-1}$ and reduces to 222 $mg_{co2}g_b^{-1}d^{-1}$ when biomass content increases by $0.5\text{-}31g_bL^{-1}$ and 5.6% consumption rate of CO_2 shows that *Scenedesmus* was not limited by availability of CO_2 concentration above 3.8% and about 90% of C-CO_2 was been utilized for growth of *Scenedesmus* (Cabello *et al.,* 2017).

Aeration and Mixing

Physico-chemical related factors termed as abiotic such as mixing/aeration, illumination, CO_2, temperature, pH and salinity and biotic factors as specie competition affect the growth of microalgae (Agarwal *et al.*, 2019; Larsdotter, 2006; Singh and Singh, 2014) and subsequent wastewater treatment efficiencies. As such mixing and aeration resulted in organic matter degradation by aiding respiration in organisms, provision of homogeneous nutrients distribution (Komolafe *et al.*, 2013) and CO_2, preventing photoinhibition (Mohammed *et al.*, 2014) and light limitation as well as enhancement of mass transfer that discourage the anaerobic gradient formation (Agarwal *et al.*, 2019).

Excessive exposure of biomass surfaces to light referred to as photoinhibition and insufficient light to the algal cells by effect of self-shading or higher turbidity of the culture termed as light limitation, which all influence the microalgal growth and productivity may be prevented by the provision of an efficient mixing (Appelberg, 2013; Larsdotter, 2006). Some biomass promotes the exchange of gases such as CO_2 and O_2 (Brennan & Owende, 2010), as such referred to as bioflocculants that triggers enzymes in the secretion of biopolymers products by extracellular mechanism.

Aeration usually provided by the use of a pump connected to the reactors with the help of a PVC pipes with smaller diameter to supply air to system, sometimes through aquaballs (Arnas, 2014; Komolafe *et al.*, 2013), while agitator or stirrer was mechanically provided centrally in the reactors which is fixed from the top to serve for efficient mixing and distribution of substances and substrates in the cultivation media and prevent settling (Anbalagan *et al.*, 2016). Efficient mixing was achieved using an overhead mechanical stirrer at rate of 100±1rpm (Mohammed *et al.*, 2014a), 110rpm (Anbalagan A., Schwede S., Lindberg C., and Nehrenheim, 2016) and 200rpm (Burakov *et al.*, 2018).

Some reported research tried to distinguished the effect of agitation and aeration in a treatment system, as Benítez *et al.*, (2018) reported a removal of N and P using a local microalgal strain with consideration of the effect of agitation and aeration. The result shows that in the PBR for agitation and aeration, the NH_4^--N and PO_4^{3-}-N removal efficiencies were 52.6 and 55.6% and 67.0 and 20.4%, respectively. In a similar development, a complete nitrification process was observed without aeration by (Arashiro, 2015) to support the assertion that in a treatment system the stirring or agitation was more efficient than the aeration alone systems.

COD Removal

COD is the determination of equivalent O_2 as part of organic matter in a simple way, which can be oxidized by active oxidant chemically and this is essential, and quickly used in determining some parameters in liquid effluents and wastewater remediation approaches. It also measures organic materials that were not part of the immediate biochemical loads on the O_2 properties of the water in the natural water course. Result from COD and BOD determination in the wastewater treatment by Pandi *et al*, (2009) showed significant reduction in COD level while that of the BOD was very low.

This may be in respect of insufficient organic loading rate associated with the wastewater and therefore, a little BOD removal efficiency was observed and substantial COD reduction as a result of organism removal of chemical compounds. Goswami and Mazumder, (2013) treated composite tannery wastewater in a batch ASP reactor using a mixed microbial consortium collected from common treatment plants. The study revealed 60% COD removal at an optimum pH of 7 and temperature of 30^{o}C from initial concentration of between 1500-6500 mg/l and optimum removal efficiency was recorded as 74%. But a higher COD removal of more than

75% was reported by Mohammed, (2013) when domestic wastewater was mixed with activated sludge in STPBR with CO_2 supplement and illuminated with red LEDs. However, 55 and 90.6% COD removal efficiencies were reported by Solé-Bundó et al., (2018) and Sun et al., (2019) respectively.

Hydraulic Retention Time (HRT)

HRT was found to be among the essential factors which can influence microalgal productivity and also affect microalgal wastewater treatment efficiency (Larsdotter, 2006). Some researches indicated that 4day HRT was essential for efficient removal of pollutants and nutrients in photobioreactors (Larsdotter, 2006; Mohammed *et al.*, 2014a), at low and moderate concentrations of wastewater. It was also indicated that longer HRT may be outranked in obtaining sufficient treatment of pollutants. Moreover, higher HRT increases the significance of the treatment. On the other hand, solid retention time (SRT) being average time the activated sludge solids are in the system, SRT is an important design and operating parameter for the activated sludge process (Anbalagan *et al.,* 2016; Luo, *et al.,* 2016). Too low SRT signifies incomplete denitrification, elevated N in treated effluent and higher chemical usage in denitrification filters, while too high SRT increased oxygen requirements and energy usage (Smith *et al.,* 2013) and so, a moderate SRT may be more suitable in order to avoid the two extreme conditions.

Biosorption

Biosorption process is categorised into physical adsorption in which the intermolecular attractive forces resulted in precipitation of adsorbent to molecular scale pores from the solution (Aljaberi and Mohammed, 2018). This occurs as a result of force of attraction between adsorbate and adsorbent (Abas *et al.*, 2013) as weak forces of Van der Waals. On the other hand, chemical adsorption involves reactions chemically between adsorbate and adsorbent (Bhatnagar & Sillanpää, 2010) with formation of a new electron bond as covalent and/or ionic as a result of the strong interaction by adsorbate and adsorbent in the medium (Gadd, 2009). Moreover, the nature and concentration of the adsorbate, ionic affinity of the adsorbent surfaces as well as characteristics of the solution influence the biosorption efficiency.

The decrease in biosorption of metals ions in the presence of comparatively light metals with corresponding charges has verily been referred to cellular binding sites for competition. A study shows that monovalent cations (H^+, Na^+, K^+) are more preferentially involved in the process of ion exchange with the biomass than the divalent ions as Cu^{2+}, Ni^{2+} and Ca^{2+} (Bilal *et al.,* 2018) and this issue of selectivity among the heavy metal cations (Rezaei, 2016), will be much less removed as the valency increases as in the case of trivalent and hexavalent cations and can be seen clearly in the results of biosorption conducted by Subashini and Rajiv, (2018) in which removal efficiency of Cu = 71%, Zn = 50%, Fe = 45% while only 40% of Cr was removed.

Ajayan *et al.,* (2015) have reported a proof in mutual interference between Ni^{2+} and Cu^{2+} on to the *C. vulgaris*. The removal of Zn was accomplished principally by heavy metals ions adsorption on to the algal cell surface. It has been delineated that first barrier to metal ions uptake was cell wall and that adsorption at surface of the cell is a significant defence mechanism that ultimately authorize extensive concentration of toxic metal ions tolerance by algae to the surrounding medium.

Mechanism of Biosorption

Algal cell wall comprised mainly of proteins, lipids and polysaccharides that host numerous negatively charged functional group such as hydroxyl, carboxyl, amino, sulfhydryl and phosphates that brought extreme affinity to bind positively changed metal ions in the solution (Ajayan *et al.,* 2015), which can be either by uptake or extracellular accumulation, sorption through surface of the cell or complexation, due to the mixture conditions and intracellular accumulation through cytoplasm and vacuole. In other word, Ojanen *et al.,* (2017) affirmed that, the metal ions uptake takes place either through active transport by surface of the cell or via endocytosis supported by the chelation of metal protein. It was believed that smaller microalgal cell have considerably larger surface area for heavy metals binding than bigger algal cells and as such *Chlorella sp.* found to be the best option.

Mechanism for efficient metal ions removal from effluent by algal cells is connected to their superior affinity to binding (Bishnoi and Nagpal, 2005; David *et al.,* 2009) and relatively larger surface area to volume ration (Hammouda *et al.,* 2015). Remarkable metal ions uptake in bioremediation may be in connection to transportation ability of metals via cell by the influence of active enzymes, and then the intracellular polymer matrix hosting the functional groups contributed to the sorption process. Intercellular polyphosphates in live algal cells that take part in the sequestration of metal ions as well as extracellular polysaccharides in algae that exert the chelation or metal binding (Ajayan *et al.,* 2015).

Heavy Metal Biosorption

Several biosorption mechanisms ware tested using microalgal species to remediate heavy metals especially in the industrial effluent due to its quantity and frequency of production coupled with increasing water shortages globally. Ozturk *et al.,* (1999), conducted a research on the biosorption of heavy metals by *Chlorella v* and *Scenedesmus o* in synthetic wastewater which treat wastewater with concentration up to 250 mgL^{-1} and the optimum biosorption were determined at pH of 5.0, 4.5 and 2.0 for copper, nickel and chromium respectively and with Cr uptake for *Chlorella sp.* and *Scenedesmus sp.* at 23.0% and 15.6% respectively.

This lower metal ions uptake calls for more investigations and Bulgariu and Bulgariu, (2014) employed the use of marine green algae (*Ultra lactuca*) treated with NaOH bioremediate metal ions contamination. The findings suggested that the biosorption increases with increasing amount of NaOH up to 0.6 $molL^{-1}$ with corresponding removal efficiency of Pb (II), Zn (II) and Cd (II) as 11.75%, 60.64 and 62.53% respectively and beyond this alkaline concentration for the treatment the biosorption efficiency remain constant.

Scenedesmus sp grown in tannery wastewater (TWW) diluted with different proportions as 10, 25, 50, 75 and 100% using distilled water. The highest growth rate was found in 50% TWW to be 1180x104cells/mL with consequent maximum metal biosorption of 81.2-96, 73.2-98 and 75-98% for Cr, Cu, Pb and Zn respectively, while more than 44.3% nitrate and 95% phosphates removal was achieved (Ajayan *et al.,* 2015). Sibi, (2016) reported that the biosorption capability is highly pH dependant and obtained an elevated removal efficiency of 63.2 mg/L at pH of 2.0 and maximum removal of Cr was at 81.3 mgL^{-1}.

Consequently, Rezaei, (2016) also observed that at pH of 5.0, the highest biosorption by *Spirulina sp* was 90.91mg/g and a greater efficiencies of 98, 98, 99 and 88% was attained for Cr, nitrates, phosphates and BOD respectively and this can be attributed to algal-bacteria impact and that the growth of Scenedesmus was proportional to the dilution with greater biomass in undiluted wastewater. A higher bio-removal of 97.15% Pb and 97.48% Cd was recorded when algal strain *Eichhornia sp* treated at a span of 15min of exposure to the contaminants with subsequent ultra-structural changes in the leaf as rapture and/or disappearance of plasma membrane, ill-functioned chloroplast and swell of mitochondria (Shalaby *et al.,* 2019).

Furthermore, Subashini and Rajiv, (2018) reported removal efficiency from tannery wastewater only, using *Chlorella v.* with removal efficiency of Cu = 70%, Zn = 50%, Fe = 45%, Cr = 40% and Ni = 20%. But a similar study by Hammouda *et al.,* (2015) showed a higher removal of 56.3% of Cr by *Chlorella v.* when tannery wastewater was mixed with domestic wastewater and also a more higher removal efficiencies was reported by Mohammed, (2013) due to the mixture of municipal wastewater with activated sludge which increases the bacterial activities in the treatment systems favouring the production of CO_2 for photosynthesis as well as O_2 for degrading waste substances (Hammouda *et al.,* 2015; Mohammed, 2013; Rezaei, 2016).

Treatment Enhancements

Based on the above submission, it can be observed that the biosorption treatment with microalgae alone has less or limited bioremediation efficiencies as reported by Ardila *et al.,* (2017); Ozturk *et al.,* (1999); Subashini and Rajiv, (2018) and with corresponding higher metal ions and nutrients removal by Mohammed, (2013); Hammouda *et al.,* (2015); Rezaei, (2016); Shalaby *et al.,* (2019) due to the mixture of microalgal species and other microorganisms sources as in domestic wastewater or activated sludge especially bacteria which contain functional groups that contributed to the heavy metals uptake, utilization of nutrients with consequent enhancements of the treatment.

Future Perspectives

Moreover, numerous researches show that these additional microorganisms specifically bacteria are capable of absorbing toxic heavy metals through their cell surface (Hochschule, 2014; Swamy *et al.,* 2009) transported in to the cell by energy transporters and eventually accumulated and converted to non or less toxic, insoluble specie with the help of nucleic acid under influence of pH and temperature (Igiri *et al.,* 2018) and this process is termed as biotransformation. Jobby *et al.,* (2018) reported the capacity of bacterial cells to biotransform the highly toxic Cr(VI) which was found to be teratogenic, mutagenic and carcinogenic to a less toxic, immobile and insoluble Cr(III) which can be removed easily from the solution than the highly toxic, soluble and mobile Cr(VI). This will enhances the bioremediation efficiencies of the microalgal treatment of heavy metals from the industrial wastewater as such should be encouraged.

In addition to that, bacterial cell can degrade nutrients mainly nitrogen compound to a less complex to a readily available form as ammonium and nitrates for microbial assimilation (Kube *et al.,* 2018) with consequent growth through the action of nitrifying and denitrifying organisms (Brannon *et al.,* 2017) which in turn increases the nutrients uptake, assimilation and utilization in order to mitigates the pollution of the natural water course with algal bloom that is termed as eutrophication which is considered to be a global menace (Zhu *et al.,* 2018). This may be connected to the higher removal efficiencies between 90-98% of algal-bacterial treatment systems as reported by Solé-bundó *et al.,* (2019); Sun *et al.,* (2019); Zhu *et al.,* (2018). Lastly, an efficient algal-bacterial ratio in the treatment, microbial biomass application as feedstock for other valuable energy option as well as recovery and reuse of biomass and heavy metals need to be thoroughly investigated.

CONCLUSION

Based on the global industrial growth, limited supply of freshwater sources coupled with the persistent nature of pollutants in industrial effluents to the ecosystem, a cost effective, environment-friendly and sustainable treatment approach is required. Microalgae were found to be best option as they grow in wastewater, sequester CO_2, assimilate nutrients, utilize available light to grow, regenerate within short period, adsorb heavy metals and accumulate pollutants. Several potentials of microalgae for bioremediation of heavy metals and other pollutants were discussed and possible enhancements of the approach are also suggested for the complete development of a sustainable treatment option. Challenges associated with hybrid microalgae-activated sludge systems was also highlighted.

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