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Utilization of Agricultural Waste Through Conventional Technologies for the Treatment of Industrial Effluents: A Review

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ABSTRACT

Agricultural waste products are commonly distributed and they are inexpensive and biodegradable. This review focuses on various agro wastes used in the treatment of industrial wastewater. As heavy metals are considered as a global threat affecting biological lives, ways to remove them from waste water are challenging. Various conventional methods are used in recent times for the removal of heavy metals from industrial waste water. Agricultural waste is a good resource for the adsorption of the dyes generated during industrial processing. The adsorption process serves as an alternative method to treat wastewater. The study provides the steps followed in various industries and explains the steps in which the toxic heavy metals find their way to the environment. This review focuses on the comprehensive ways of utilization agro wastes as good treatment material which are also eco-friendly. The review suggests how agro wastes form a potential, effective, affordable and sustainable sorbent biomaterial for minimizing environmental pollution.

Key words: Agricultural Waste, Conventional methods, Industrial effluents, Metal removal Ions.

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Agricultural wastes are derived from plants and can be effectively converted into organic fertilizer or burned when favorable conditions exist. These wastes, along with harvested biomass, offer a renewable resource in the form of agricultural biomass. Biomass is abundant, energy-dense and can be transformed into new resources, providing renewable biological chemicals and energy with minimal negative environmental impact (Pasin *et al*., 2020). The availability of biomass in nature promotes both environmental sustainability and economic development (Srivastava *et al.,* 2021; Niphadkar *et al*., 2018). However, utilizing agricultural waste poses a significant challenge (Loeppert *et al*., 1996). The global industrial development and population growth have led to significant heavy metal pollution, disrupting natural ecosystems through their discharge into land and water (Saravanan *et al*., 2021) (Fig 1). Converting agricultural waste into an energy resource is an effective way to eliminate it from the environment and create a source of renewable energy (Xie *et al.,* 2019). Agro-waste products such as sawdust, sugarcane bagasse, rice husk, neem bark, coconut husk and oil palm shell are utilized for removing heavy metals from industrial effluents in various industries that employ adsorption technologies Hala (Ahmed *et al*., 2013).

Agro-waste products can also serve as binding agents in concrete cement. Various energy utilization technologies for agricultural waste include gasification, thermal cracking gas, liquefaction (enzymolysis, hydrolysis, water phase catalysis and Fischer-Tropsch synthesis), solidification (steam explosion pretreatment and biomass briquette), power generation (direct straw burning, biogas generation) and straw coal co-firing (Lam *et al.,* 2015; Chih-Chun *et al.,* 2015). Heavy metals such as cadmium (Cd), copper (Cu), arsenic (As), chromium (Cr), zinc (Zn), lead (Pb), nickel (Ni), manganese (Mn) and mercury (Hg) are major pollutants in freshwater. These metals are toxic, non-biodegradable and persistent in nature (Babarinde *et al*., 2006). Developing countries typically employ advanced technologies like vacuum evaporation, ion exchange resins, crystallization, membrane technologies and solvent extraction to remove heavy metal toxicity from wastewater (Regel *et al*., 2010). Conventional methods for eliminating heavy metals include chemical precipitation, reverse osmosis, filtration and electrochemical treatments such as ion exchange, redox reactions, evaporation and adsorption. However, these methods are often ineffective and costly to operate (Giraldo *et al*., 2008). Researchers are now focusing on developing low-cost and safe alternatives. Table 1 provides an overview of various conventional methods. Concrete, composed of aggregates, cement, reinforced steel bars and water, finds applications in construction, transportation, hydraulics and the military sector (Yin *et al*., 2015).

Agricultural waste materials can serve as alternative aggregates in construction but typically do not contribute significantly to supplementary cementitious materials (Liew *et al.*, 2017). According to Ismail *et al.* (1996), numerous studies have demonstrated that agricultural waste possesses a substantial quantity of amorphous silica, making it suitable for use as a partial replacement (10-30%) of cement in concrete. Aromatic compounds like phenols, which are toxic and commonly found in industries such as coal, petroleum refining and plastics, can be effectively removed from aqueous solutions using activated carbons derived from pine bark, apricot stone and rubber seed coat. Rengaraj *et al.* (2001) stated that activated carbons derived from agro-wastes present a viable and economical approach for the removal of pollutants.

Conventional methods for removal of heavy metals

Adsorption

Adsorption is a recognized method for the elimination of heavy metals from wastewater. The adsorption process produce high-quality treated effluents. Compared to other wastewater treatment techniques, adsorption technology offers a greater advantage. By adsorbing the ions through the affinity filter, ion exchange processes are selective to the particular ions (Weber *et al.*, 1972). The adsorption phenomenon takes place between two interface such as solid-liquid, liquid-solid, solid-solid and liquid-liquid. Recent studies showed increased interest in the use of these biomaterials as adsorbents for adsorption of copper by Spent yeast Apinthanapong *et al.* (2009), adsorption of Copper ions from aqueous solution onto iron oxide coated egg shell powder (Areco *et al.*, 2010).

Ion exchange

The ion exchange method is the most promising technology which eliminates important metal ions from the industrial wastewater. In the ion-exchange process, the ion exchange resins are used. This technology uses either synthetic resins or natural resins to exchange the specific cations in the wastewater. Mainly synthetic resins are used in the ion exchange method for the effective elimination of heavy metal ions from the solution (Alyuz *et al.*, 2009). The ion exchange method is a well-developed process, but to keep it efficient in removing the intended pollutants from wastewater, the resins that are employed need to be periodically renewed.

Chemical precipitation

Chemical precipitation is the most commonly employed technique used for the elimination of heavy metals from wastewater. It mainly involves adding a precipitating reagent to the polluted wastewater which converts the dissolved metals into solid particles. The particles from the wastewater get aggregated by chemical coagulation and are finally removed by filtration or sedimentation. Bivalent metals such as Cu (II), Cd (II), Mn (II) and Zn (II) can be removed by this chemical precipitation method. During this method, the pH is adjusted with alkaline reagents. Chemical precipitation is usually used to treat wastewater containing high concentrations of heavy metal ions and it is ineffective when metal ion concentrations are low or they settle down (Alvarez-Ayuso *et al.*, 2003).

Membrane filtration

Membrane filtration experiments were conducted to assess the rejection rates of aluminum, nickel and chromium at different operating pressures using various membrane types: ultrafiltration (UF) at 5 and 7.5 bar, nanofiltration (NF) at 10, 15 and 20 bar and reverse osmosis (RO) at 10 and 20 bar. These membrane filtration processes have shown promise in effectively removing metals due to their high removal efficiency, ease of operation and minimal space requirements (Nuray *et al.*, 2018). In addition to aluminum, nickel and chromium, membrane filtration is widely recognized as a leading method for the removal of other heavy metal ions such as cadmium (Cd^{2}+), lead (Pb^{2}+), copper (Cu^{2}+) and mercury (Hg^{2}+) from wastewater Ercarikci *et al.* (2020).

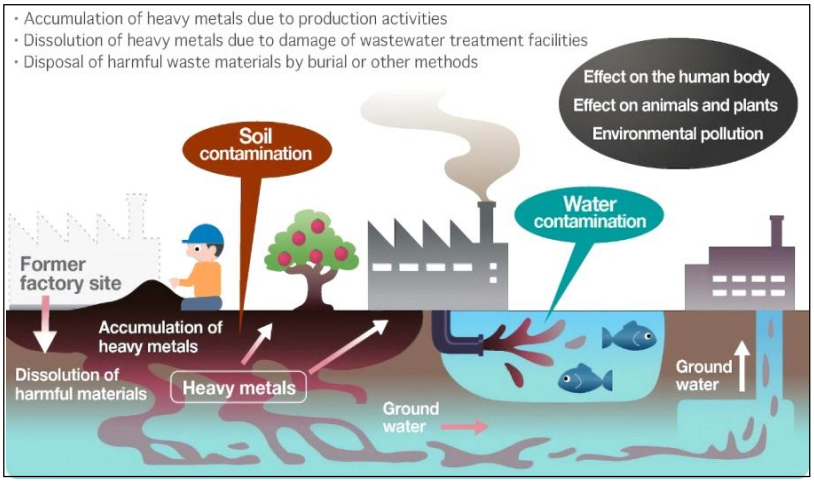


Fig 1: Heavy metal pollution and contamination in water and soil.

Reverse osmosis

Reverse osmosis utilizes a semipermeable membrane and operates on the size exclusion and solution diffusion principles. The mechanism is by passing water through the polymer material membrane having netted structure (Greenlee *et al.*, 2009). Reverse osmosis is the reverse procedure of osmosis, where the solvent travels from a lower concentration to a higher concentration where no external pressure is applied.

Nanofiltration

Nanofiltration is the pressure-driven membrane separation process that is often used for separation of heavy metals (Monovalent and Divalent Ions). Reverse osmosis membranes have pores with a range of 1 to 10 nm, while nanofiltration membranes have slightly larger pores. Nanofiltration is a promising technology for elimination of heavy metals because of its low energy requirements, high efficiency and easy operation Murthy *et al.*, 2008).

Ultrafiltration

The ultrafiltration method is employed to increase the size of the species in order to separate heavy metal ions from wastewater. It is a low-pressure technique and the membrane's pore span from 0.003-0.1 m in size (Vishali *et al.*, 2021).

Table 1: Various conventional methods and their material characteristics.

Processes	Materials used	Advantages	Disadvantages
Chemical precipitation	Alkali, lime, surfactants, sulfide/flocculants, acids	Feasible technique, large amounts of wastewater can be handled with this method, easy to use.	Require more chemicals, maintaining lot of variables are challenging.
Ion exchange	Ion exchange resins (Synthetic or natural)	High treatment capacity and greater metal removal rates.	Not cost effective.
Membrane filtration	Surfactants	Effluent limitation can be reduced by reusing wastewater, recovering valuable materials and preventing environmental harm.	When the concentration of metal ions is lower, membrane fouling happens, Capital costs, maintenance costs and operating costs are more.
Coagulation/fiocculation	Reagent slike salt sofiron, aluminum	Applicable to the treatment of large-scale wastewater	Costly chemicals, a lot of sludge being produced, sludge disposal issue.
Electrolytic recovery	Electrical metals	Efficient removal of the metal.	Costly and decreased efficiency at low concentrations. This method can't be used with larger wastewater.
Adsorption	Pumps, fluid handling equipment and regenerators	Extremely efficient at reducing heavy metals to acceptable levels.	High expenses are associated with the manufacture of adsorbent, for a steady, uniform flow. the need for chemical regeneration, fouling and corrosion of the treatment plant, disposal of used adsorbents.
Reverse osmosis	Membrane-supported resins	Effective	High chemical expenses and membrane fouling.

Table 2: Metal ions adsorbed using various agricultural adsorbents.

Agricultural wastes used asbio-absorbents	Experimental media	Extractable metals
Waste fruit cortexes	Water	Cd^{+2},Zn^{+},Cr^{+3}
The modified shell of wild endemic almonds	Contaminated water	Ni, Cr(VI),(III)
Rice husk and fly ash	Wastewater	Fe, Pb, Ni
Watermelon shell	Aqueous solutions	Cu
Natural and modified rice husk	Aqueous solutions	Cd(II)
Pre-treated rice husk	Aqueous solutions	Cd
Tea factory waste	Aqueous solutions	Ni
Tea-industry waste	Aqueous solutions	Cu, Cd
Grape stalks wastes	Aqueous solutions	Cu

The separation of contaminants from sewage is accomplished by electrostatic and hydrophobic forces. When surfactants are added in excess during the ultrafiltration process, aggregates are formed so that membranes cannot pass through (Samper *et al.,* 2009).

Coagulation/Flocculation

The coagulation/flocculation comprises of two steps: the first step destabilizes the particles and the second step aggregates (flocculates) the destabilized neutral particles. The wastewater stabilized with coagulants like alum and colloids forms big flocks that can be easily removed by the sedimentation process (Kurniawan *et al.*, 2006).

Flotation

Flotation is the separation technique of liquid emulsions and suspensions detached from the dispersed phase. Dissolved air flotation, ion flotation and precipitation flotation are the three primary flotation techniques used to eliminate metal ions from wastewater (Sudilovskiy *et al.*, 2008).

Agricultural adsorbents for industrial effluents

Adsorbents for industrial and agricultural use those are effective at removing heavy metals from wastewater are listed below. Table 2 explains agricultural waste and its suitable extractable materials (Parisa *et al.*, 2018).

Rice husk

Rice husk is considered to be a major agricultural waste in rice-producing countries as the production is approximately 50 million metric tons. Dry rice husk contains 70-85% of organic matter (lignin, cellulose, sugars, *etc*.) and silica, which is present in the cellular membrane of rice husk (Vempati *et al.*, 1995). The unmodified or modified rice husk acts as the best adsorbent for the removal of pollutants. The study revealed that the removal efficiency of Cd(II) and Zn(II) ions significantly improves with increasing pH beyond 2. Interestingly, at pH levels greater than 8.0, the uptake of these metal ions reaches 100%. These findings demonstrate the strong influence of pH on the sorption process, indicating that higher pH conditions favor the adsorption of Cd(II) and Zn(II) from the solution. The modified rice husk is potentially a useful material for the removal of copper and lead from aqueous solutions (Wong *et al.*, 2003). Table 3 summarizes the cadmium removal using modified rice husk.

Fly ash

Fly ash is a naturally occurring sedimentation material of coal produced from the combustion of coal in power plants (Fig 2). It is generally extracted by the precipitators in the smokestacks of coal-burning power plants to reduce pollution and fly ash has a capacity as a soil stabilizer and structural concrete admixture (Marshall *et al.*, 1999).

Sugarcane bagasse

Sugarcane bagasse is an agricultural waste composed of cellulose (50%), polyose (27%) and lignin (23%) (Fig 3) (Hanafiah *et al.*, 2008). Acinetobacter haemolyticus from sugarcane bagasse is typically employed as a bio-adsorbent to remove the chromium. This bacteria reduces chromium (Cr) to chromium (III), which is less poisonous and soluble than chromium (VI) and removal of more than 90% was achieved (Ahmad *et al.*, 2013). Using zinc chloride,

Table 3: Cadmium removal using rice husk as an adsorbent.

Adsorbent	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorption capacity (mg/g)	Removal percentage (%)
Rice husk ash	10-100	6	Redlih-peterson, freundlih	5	1-10	3.04	29.8%
Sulphuric acid Treated rice husk	50,100	4	Langmuir	60	1.0	38.76 and 41.15	–
Activatedrice husk	8.9-89 M	6	Dubinin-radush kevish and freundlih, langmuir	20	4.0	-	97%

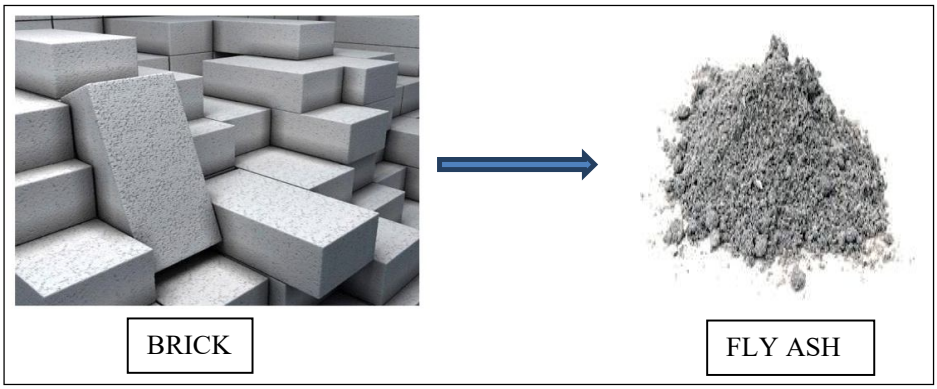


Fig 2: Fly ash produced from brick.

chromium was extracted from the activated sugarcane bagasse and >87% chromium was removed at an ideal pH of 8.58 (Cronje *et al.*, 2011).

Coconut husk

Coconut waste acts as an adsorbent for chromium removal and its sorption properties are due to the presence of coordinating functional groups such as hydroxyl and carboxyl (Tan *et al.*, 1993). Coconut coir pith was the best adsorbent for removal of heavy metals (Fig 4). The modified coir pith of coconut waste using the surfactant hexa decyl tri-methyl ammonium bromide was used for chromium removal. The maximum removal obtained with this material was reported as 76.3 mg/g (maximum adsorption capacity). The study showed that the coconut waste coir pith has higher adsorption removal than other agricultural adsorbents (Sumathi *et al.*, 2005).

Wheat bran

Wheat bran is a by-product of wheat obtained from the shell of flour mill (Fig 5) and is used for the removal of heavy metals (Kaya *et al.*, 2014). The functional groups such as methoxy, phenolic hydroxyl and carbonyl will help to bind heavy metals and have demonstrated the removal of chromium using wheat bran with a maximum adsorption capacity of 93 mg/g and a maximum removal of 89% (Ravat *et al.*, 2000).

Coffee residue

Coffee grounds act as an adsorbent to take cadmium out of industrial wastewater. Clay was combined with agricultural waste, such as coffee grounds for heavy metal removal. This creates an efficient adsorbent with a negative charge that encourages cadmium complexation and its removal (Boonamnuayvitaya *et al.*, 2004). Azouaou *et al.* (2010) stated that that cafeteria garbage is utilized as a bioadsorbent for the removal of cadmium, with a reported adsorption capacity of 15.65 mg/g, 80% of cadmium was found to be removal at a pH of 7. Fig 6 shows the elimination of cadmium metal from industrial wastewater (Arao *et al.*, 2010).

Modified saw dust

Sawdust is a solid waste that is generated in significant amount at sawmills (Fig 7). Saw Dusts are used as an adsorbent material for the removal of heavy metals from wastewater (Shukla *et al.*, 2002). Saw dust of oak blended with hydrochloric acid is used for elimination of chromium from industrial effluents (Argun *et al.*, 2007). Pine sawdust as a modified form was used for removal of chromium at an optimum pH of 2 (Politi and Sidiras, 2012).

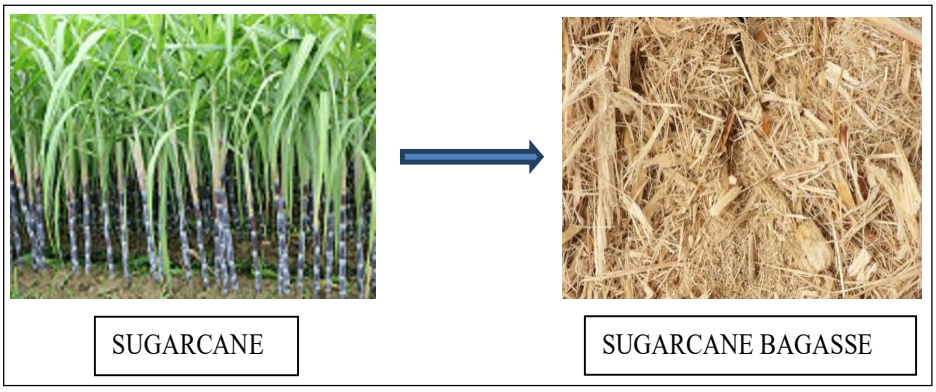


Fig 3: Bagasse produced from sugarcane.

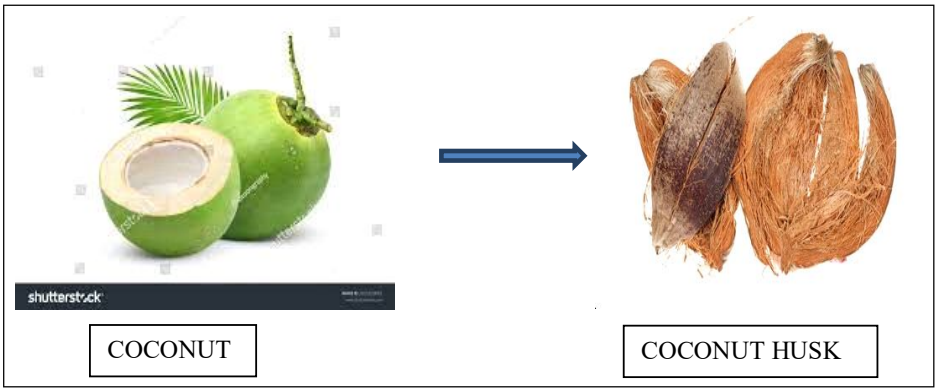


Fig 4: Coconut Husk produced from Coconut shell.

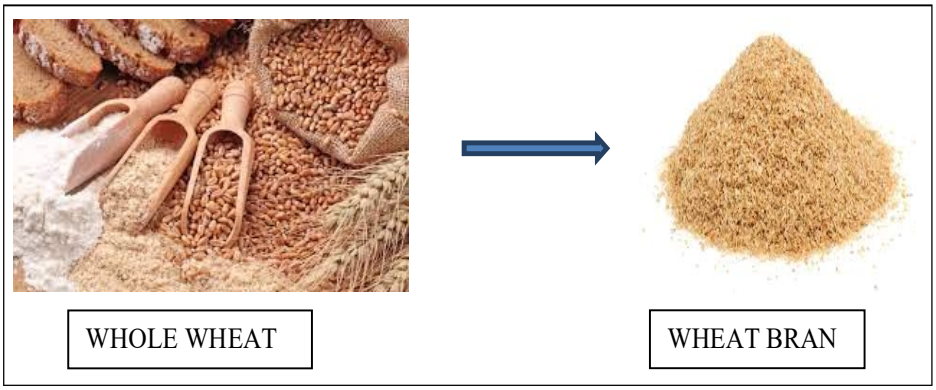


Fig 5: Wheat bran is obtained from whole wheat.

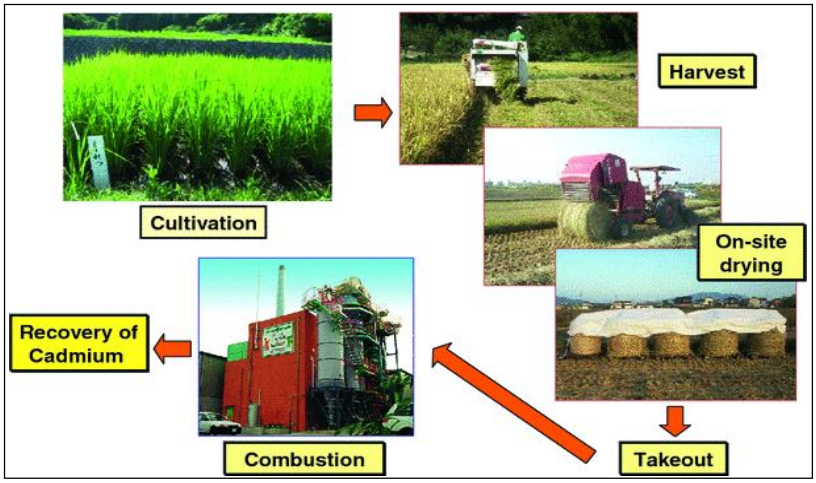


Fig 6: Cadmium removal from agro waste.



Fig 7: Saw dust is a by-product of wood log.

CONCLUSION

The disposal of millions of tons of agricultural biomasses as waste each year presents a significant environmental challenge. However, these biomass materials hold great potential as valuable resources, particularly in the realm of energy production and heavy metal remediation. Through various conventional methods such as adsorption, ion exchange resins, chemical precipitation, coagulation, solvent extraction and membrane filtration, researchers have explored the use of bio-adsorbents derived from agricultural waste to effectively remove toxic heavy metals from wastewater. Adsorption, a process heavily influenced by factors such as surface chemistry, pH, charge distribution and metal ion concentration, plays a crucial role in the

efficiency of heavy metal removal by bio-adsorbents. Ion exchange and complexation are the major mechanisms involved in the uptake of metals by these materials. Common agricultural waste bio-adsorbents include rice husk, coconut husk, sugarcane bagasse, wheat bran and coffee residue. These materials possess high adsorption capacities, are readily available in large quantities and exhibit mono to multilayer adsorption behavior, making them attractive alternatives to conventional adsorbents. Numerous studies have demonstrated the efficacy of agricultural waste bio-adsorbents in removing heavy metals such as chromium, cadmium, copper and lead from wastewater. Optimal pH ranges for efficient removal have been identified, with pH 1-2 suitable for chromium, pH 4-7 for cadmium and pH 4.5-6 for copper. Furthermore, bio-adsorbents offer advantages such as their low cost, abundant availability, minimal sludge generation, technical feasibility and strong affinity for heavy metals, making them well-suited for engineering applications. Additionally, the use of membranes, particularly in reverse osmosis processes, has gained prominence in wastewater treatment. Reverse osmosis involves the movement of solvent from an area of low solute concentration to an area of high solute concentration through a dense barrier layer in the membrane. Membrane filtration can be employed alongside bio-adsorption methods to enhance the overall efficiency of heavy metal removal.

Conflict of interest: None.

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