UTILISING AGRICULTURAL WASTE AS NATURAL BIOSORBENTS – A REVIEW

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Abstract: Wastewater is way too valuable to throw away, especially in a world where there is an increasing scarcity of drinkable water. Industries like photography, electroplating, mining etc leads to inclusion of heavy metals in the waste and ground water, posing life threatening threats to all forms of life. Lack of treatment facilities for such heavy metals have deteriorated the water quality for aquatic resources, this deterioration in turn causes health problems for the masses at large. Thus, effective removal of heavy metals from aqueous wastes is among the most important issues that can be effectively tackled by using novel technologies by using fruit peel wastes. Fruit peels are rich in cellulosic materials mainly, pectin, which is structurally very much similar to alginate, found in brown algae. It is primarily known to be responsible for the uptake of heavy metal ions. This paper critically reviews and compiles the work reported by various scientists and researchers on the utilisation of fruit peels as biosorbents. The article also considers the future perspectives in the field of biosorbent development by using agricultural waste for water treatment.

***IndexTerms*:** Natural biosorbents, fruit peels, heavy metals, waste water treatment, biosorption.

1. Introduction

One of the most common forms of pollution control is wastewater treatment. The rapidly increasing population and industrialisation has resulted in huge wastewater generation and is capable of making all perpetual aquatic resources unfit for their desired uses in the following years to come [1]. Heavy metals becoming a part of wastewater are an emerging issue which needs to be resolved, in order to prevent live forms from life threatening diseases. Heavy metals are non- biodegradable, and can persist for infinite periods once they get metabolised in the food web ,their concentration gets increased in every level of the food web known as biomagnification .Various technologies are being put to use for successful removal of several heavy metals from wastewater namely, nanofiltration, ultrafiltration, coagulation/flocculation, electro flotation, chemical precipitation, electrochemical treatment, photocatalytic removal, coprecipitation, ion-exchange, and reverse osmosis[2]. However, owing to their installation and operational cost, selective removal capability and production of sludge as a secondary or tertiary waste which in turn requires an additional treatment, discourages industrialists for the use of conventional methods[3][4].

Agricultural waste peels have always been considered as an ecological burden for the society. However, waste peels, being rich in lignocellulosic materials, have opened up new ways of being used as renewable, affordable and sustainable adsorbents for water treatment applications [5][6]. It is a potential option over conventional processes for the metal ion removal because of the low cost, easy availability, reduction in the volume of chemical, and/or biological sludge to be disposed of, no nutrient requirements, flexibility in terms of operation and effectiveness in detoxifying even very dilute effluents[7][8] .

Nowadays, ***biosorption*** is emerging as a new and sustainable way of removing heavy metals from wastewater, owing to the fact that waste peels act as dead/inactive biomass to sequester heavy metals from solutions by a broad range of physicochemical mechanisms, comprising chelation, complexation, ion exchange, physical adsorption, and surface micro precipitation. The biomass utilized herein is termed biosorbent. [8] There are several ways which are reported for the processing and production of wastewater biosorbents, namely, drying, reduction of particle size and preparation of activated carbon from waste peels and pomace [9][10]. The resulting particles are fine sized, and have the capability of remaining suspended in the wastewater to be treated [11]. Adsorption which is nothing but the cohesion of ions on the outer surface, has been recognized as feasible method for heavy metals removal from contaminated water since it is cheap and eco-friendly

The high absorption efficiency of agricultural peel waste is related to many functional groups namely alcoholic, carbonyl phenolic, amino and sulfhydryl [12]. The sorption mechanism by agricultural biomass consists of following steps: Chemisorption, Complexation, and Adsorption on the surfaces and Diffusion from pores and Ion exchange. [12][13]

2. Universal Production and Productivity

Although decrease in food loss and waste seems to be of utmost importance and appears to be as a clear objective, but, somehow real implementation is not as simple as it seems to be and complete elimination of food losses looks next to impossible and unrealistic. [3][4][14]Various studies suggest that almost one-third of the total food produced for consumption is wasted globally (1.3 billion tons per year) [14]. This indirectly implies that numerous resources used in food production are getting wasted, namely fertilisers, land, water, manpower and energy [15]. Such huge food losses in turn add up to landfills load, and such emissions adds up to harmful greenhouse gases. Significant food losses and wastage happens in the initial supply chain and much less food is wasted at the consumer level [14][15][. Fruits are a rich sources of phytochemicals, and most of these lie in the wasted part of the fruit. Not just fruits but many other plant crops like, coffee for that matter are a great example, whose waste generates by-products which are rich in useful phytochemicals.

Major factors responsible for food losses and waste are:

- Harvesting techniques
- Storage
- Transportation
- Processing
- Cooling facilities
- Infrastructure
- Packaging
- Marketing systems[15][16]

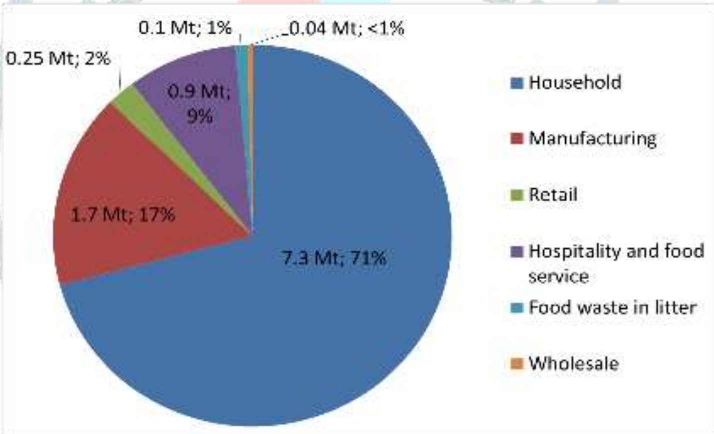

Figure 1: Amount of food waste arising by sector [17].

As far as the wastage is concerned, apples generate 10.91% of seed and pulp as by-products, and 89.09% of final products during slicing. Dicing of papaya produces about 8.5% of peel waste, 6.5% of seeds, 32% unsuable pulp, and about 53% of final product [18]. The peeling of mandarins generates about 16% of peels and 84% of finished product. Pineapple processing yields about 14% of peels, 9% of core, 15% of pulp, 15% of top, and 48% of total final product. Processing of mangoes produces about 11% of peels, 13.5% of seeds, 18% of inoperable pulp, and 58% of finished product. Moreover, juice production from fruits and vegetables produces around 5.5 MMT of waste including pomace. Grape and wine processing industries generate around 5 to 9 MMT of solid waste yearly worldwide, which constitutes 20% to 30% of processed materials. Canning and frozen industries of fruits and vegetables generate approximately 6 MMT of solid waste annually, which is composed of 20% to 30% leaves, stalks, and stems[19][20][21]

3. Impact of Heavy Metals on human health

There are several ongoing anthropogenic activities that contribute to various kinds of pollution. The emissions from these activities lead to the introduction of heavy metals in the environment [22]. Such heavy metals accumulate in soil and then make their way into water bodies steadily. The prime reason for heavy metals toxicity lies in the fact, that they are non-biodegradable and Metals like lead, chromium, mercury, uranium, zinc, arsenic, cadmium, cobalt, copper and nickel are considered to be toxic [24][23][22]. People coming in contact with lead and cadmium often suffer from renal or kidney failure and the main source of these heavy metals being contaminated water which is being served as potable water[25][26]. Lead as we all heard quite often is a dangerous element; it is harmful even in small amounts. Lead enters the human body in various ways:-

- It gets inhaled in our lungs through lead paints
- Waste gases emerging from lead induced gasoline.
- It is also found in trace amounts in fishes, which are pretty much prone to industrial pollution. [26][27]

Exposure to lead is cumulative over time and high levels of lead in human system may lead to death or serious damage to the central nervous system, the brain or kidneys, it may also lead to problems like hyperactivity and various learning problems, anti-social behaviour in children[27][28][29].

Various studies have shown that water contaminated with nickel and chromium leads to hair loss. No doubt nickel is an important trace element but is heavily toxic and is considered to be carcinogenic to human. Another notable point is that, nickel's toxicity increases in the presence of other metals, for e.g copper, cobalt [30]. Its toxicity is enhanced in the presence of other metals such as cobalt, copper, iron and zinc in drinking water. Nickel, on the other hand is also related to various skin issues like eczema, derma toxicity and skin irritation [31][32]. Chromium is also essential to humans like many other metal ions, but is very toxic in hexavalent form. [30]On the other hand, chromium is essential to animals and human. Long and short-term exposure to chromium can lead to dermatitis, ulceration of the skin, kidney and liver damage [32][34][35]. Mercury is a known toxic and has no proven function in human physiology. Almost all forms of mercury are capable of causing abortion in expectant mothers, congenital malformation and several GI disorders like corrosive esophagitis and hematochezia[35[36][37]. Arsenic is the twentieth most abundant element on earth and its inorganic forms such as arsenite and arsenate compounds are lethal to the environment and living creatures Arsenic's toxicity on the other hand, depend on its initial chemical form ingested, and is cancer causing in all its oxidation states [38][39]. Arsenic is dangerous in a way that it coagulates protein, forms complexes with coenzymes and inhibits the production of adenosine triphosphate (ATP) during respiration[40][41]. Arsenic is a proto plastic poison since it affects primarily the sulphydryl group of cells causing malfunctioning of cell respiration, cell enzymes and mitosis.

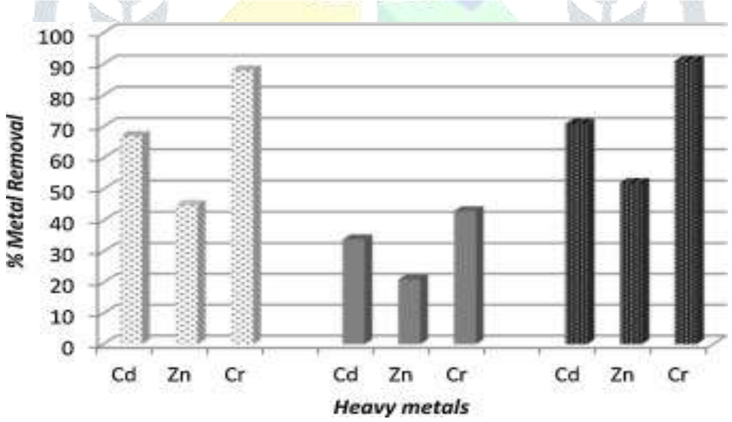

Figure 2. Removal of heavy metals from wastewater. The white bars are of pomegranate, the grey bars represent banana and the black bars shows orange peel [42].

4. Defining Factors Influencing Biosorption

The performance and capability of biosorption are gets affected by various physical and chemical characteristics of both biosorbent and sorbate. There are several factors that comes into play when biosorbents are tried to successfully be used for wastewater treatment. All such factors are further discussed in detail.

4.1 pH and Ionic Strength

It is a prime factor affecting biosorbency of any compound, as it influences not just the final charge of the functional groups attached to the biosorbent molecule, but also its solubility and ionisation degree[43]. It is so because, the protonation of functional groups and ionization degree of the biosorbent material majorly depends upon the initial pH of the aqueous solution. Several researches have proved that heavy metal uptake and high pH are directly propotional, and biosorption is largely governed by the electrostatic interactions. As pH rises from 6.0 to 7.0, the retention capacity of the adsorbing biosorbent material rises significantly. On the contrary, in lower pH the adsorption process was largely affected and decreased. At high pH, biosorption increases as more number of H_3O^+ ions leaves the biosorbent surface making the sites available for metal ions uptake. [44] [50]

4.2 Initial Sorbate Concentration

The amount of initial sorbate concentration plays an important role in efficient biosorbency, as it encourages in overcoming mass transfer resistance and has a linear correlation. Biosorbent dose is a significant factor that influences the biosorption efficiency and biosorption capacity under a given initial biosorbate concentration and operating condition.

Major Principal behind these phenomena is, as the biosorbent dose increases, the number of available active sites increases and eventually enhances the removal of toxic metal ions. [45]

4.3 Temperature

Temperature has an important role to play while dealing with wastewater effluents, as most of the time they are discharged at high temperatures due to processing. For endothermic reactions, biosorption and heavy metal ion uptake magnitude, is directly proportional with temperature, for a simple reason being, increase in surface activity and leading to availability of more active sites. But such is not the case with, exothermic reactions, because sorption rate for endothermic reactions gets enhanced as increase in temperature is actually following Arrhenius equation. [45] [46]

4.4 Particle Size of The Sorbent

The particle size of the biosorbent plays a vital role in the whole process, as with the increase in size of the biosorption material's pore size, the capacity of the material decreases. The reason being, large pores makes space for unwanted particles too, and leads to the clogging of pores. Generally, surface reaction is the governing mechanism, but sometimes, decrease in particle size has shown to improve the uptake due to increase in surface area. In addition to that, decrease in particle size encourages diffusion capacity and sorption rates since it reduces intraparticle diffusion. [46] [47]

4.5 Competition From Co-ions

In a multicomponent systems competition and interference between ions in the sorbate mixture, is yet another factor affecting biosorbent efficiency. Since there is a constant interference by the other ions present in the mixture, uptake capacity of single ion component mixture was lower with respect to their counterparts in a multicomponent ion system, thus, higher removal efficiency is there for heavy metals in a multi component system. [47]

4.6 Exposure Period

Time is an important factor to be considered in biosorption studies as it helps to eastablish the rate of biosorption and the attainment of equilibrium for a particular process. Contact time of biosorbent material and percentage attained for uptake of heavy metals is directly proportional, and has a linear correlation. Many studies have shown that, on increasing contact time of biosorbents to upto 3 hours, biosorbency got increased by almost 80% .[48] [49]

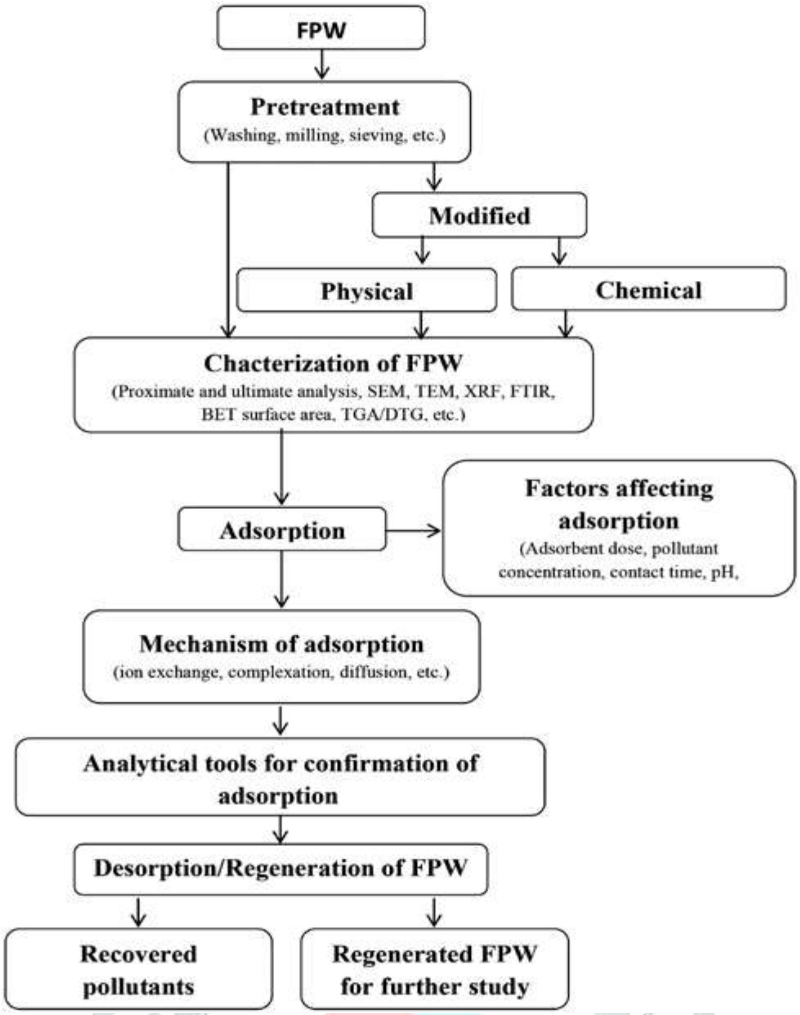

Figure 3: Overall adsorption process using FPW [51].

5. Future direction and Conclusion

India comes in the list of highest agricultural production countries, yet we lack in several processing technologies and food chain supply. Another change in pattern of food habits which we can observe in today's consumers is there inclination towards convenience foods. Over the past couple of years there has been an exponential growth in the world's population. This has eventually led to the environmental load of waste generation, heavy metals being amongst the major concern. Some metals like Zinc, magnesium, and copper are needed for animal and flora as micronutrients, however, if they accumulate in larger amounts they would become a lot unsafe if they're not treated in a proper way. For proper treatment prior characterization studies on the biosorbent may help in selecting the suitable treatment option. Biosorbency capabilities can be enhanced by various pretreatments chemical, thermal or immobilization. Another pretreatment that can be taken up is to add new functional groups to the biosorbent and it enhances biosorption.Biosorption utilizing industrial food process and pharmaceutical wastes might give a cheap, eco-friendly and viable source for treating waste matter effluents, and thereby creating a smart use of waste materials. However, additional work needs to put in to specialize in scaling up the planned biosorption processes and finding out their technoeconomic feasibleness. Analysis ought to be extended for treatment of biosorbents for various categories of contaminants like phenoplast compounds and mycotoxins.

Biosorption, as we all know, is in its initial and developmental stages, and is capable of untapping several underutilized opportunities in the coming future. Basic fundamental research should be continued and encouraged to have the better understanding of the biosorbency mechanism. We need to continue basic analysis to understand the mechanisms and bio-accumulatory processes in depth.

It is desirable to develop biosorbents with wide range of spectrum that would take away and absorb, a range of pollutants, one such method that could be adopted is the utilization of 'combo' biosorbents consisting more than one variety of biomass. Though 'combo' biosorbents would tend to probably complicate the characterization of biosorption systems, but it would might represent a practical approach towards planning and design of biosorbent systems .

Although chemical pretreatment considerably enhance biosorptive capability and specificity of the biomass, these don't seem to be cost effective at industrial scale and further study is needed to bring down the total cost for pretreatments. So far, biosorption analysis has principally aimed for the removal of pollutants like significant metals and organics. However, valuable resources like gold, platinum, palladium, ruthenium, etc have gained attention, for two simple reasons, limited resources and high price. Biosorbents may be conjointly used for the purification of ionic pharma proteins, antibodies, and peptides.

Although chemicalpretreatment methods significantly enhance biosorptive capacity and specificity of the biomass, these are not cost effective at large scale . Further study is therefore required to drop the overall cost for pretreatments or to develop new methods that are both cheap and effective. Biosorption processes are still at the stage of laboratory-scale study in spite of satisfactory progress. Thus, much work in this area is necessary to demonstrate its possibilities on an industrial scale.

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