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Agricultural wastes as low cost adsorbents for sequestration of heavy metal ions and synthetic dyes from aqueous solution: A mini review

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Abstract : Rapid industrialization has resulted in increased disposal of industrial effluents containing organic and inorganic contaminants. Various physical and chemical techniques are developed and used in practice for the treatment of effluents. Most of the techniques are limited in application due to cost, time and efficiency. Adsorption is found to be the most effective and prolific technique for the sequestration of heavy metal ions and synthetic dyes. Interestingly, agricultural waste materials are found to be most promising and effective adsorbents for the removal of contaminants. Agricultural wastes are known to be rich in functional groups which facilitate binding of cations on to the surface. The present review discusses about the various types of agricultural wastes specially focusing on fruit based waste as adsorbent for the sequestration of heavy metal ions and synthetic dyes from aqueous solution.
Keywords: Adsorption, Agricultural wastes, Heavy metal ions, Synthetic dyes.

Introduction

Rapid industrialization has resulted in the increased disposal of effluents loaded with heavy metal ions and organic contaminants. The effluents loaded with contaminants are let into rivers and water receiving bodies. Industries such as electroplating and battery manufacturer’s discharge huge amount of effluents into environment loaded with high concentrations of heavy metal ions. Similarly, textile and dyeing industries discharge colored effluents which disturb the aesthetics of quality of water. The presence of heavy metal ions in drinking water can cause damage to nervous system, lungs, kidneys and liver. Colored water due to the presence of dyes causes dizziness, mental confusion, skin diseases and bladder irritation. It has been observed that water pollution is the leading worldwide cause of deaths accounting over 14,000 people daily. In India, an estimate of 580 people die every day due to water pollution related diseases and illness. Hence, treatment of industrial effluents loaded with heavy metal ions and synthetic dyes are desirable.

Various treatment techniques are developed by many researchers for the remediation or removal of heavy metal ions and synthetic dyes from aqueous solution. Techniques include oxidation/reduction, precipitation, ion exchange, reverse osmosis, membrane filtrations, electrochemical treatment, flotation, coagulation, adsorption and biological treatment. Although many treatment techniques are available, adsorption are found to be the most effective and prolific methods. Adsorption is found to be the cost effective technique with ease for regeneration of adsorbents with proper desorbing agents. Activated carbon, nano adsorbents are found to be effective and prolific adsorbents but, the cost of activation and regeneration of used carbon and synthesis of nanomaterials limits the application in commercial stage. Hence a brief literature review was carried out to consolidate the low cost adsorbents employed till date with special focus on agricultural waste based adsorbents.

Low cost adsorbents

Agricultural wastes and by products were found to be low cost and alternate adsorbents for the removal of heavy metal ions and dyes. Agro wastes are rich in organic contents with variety of functional groups which can cooperate binding of cations and anions. The other advantages of agricultural wastes are easily available, non-hazardous and no disposal problems. Several agricultural wastes have been studied and reported for the removal of heavy metal ions and dyes.

Rice husk

Rice husk, a major agricultural by product was found to have affinity towards heavy metal ions and synthetic dyes. Roy et al[1] studied the removal of heavy metal ions such as Pb^{2+}, As^{5+}, Cd^{2+} and Cr^{6+} from aqueous solution. Bishnoi et al[2] studied the removal of Cr^{6+} from aqueous solution by rice husk activated carbon and the removal efficiency was found to be high compared to raw husk. Ajmal et al[3] studied the feasibility of pretreated rice husk for the removal of Cd^{2+} ions from aqueous solution and was found to be better than raw husk. Various pretreatment of rice husk was studied by many researchers for enhancing the loading capacity of rice husk towards metal ions. Mckay et al[4] studied the removal of methylene blue and basic red from aqueous solution with raw rice husk and loading capacity was found to be 312 mg g^{-1}. Kannan and Sundaram[5] reported the use of activated carbon rice husk for the removal of methylene blue and found higher loading capacity compared to raw husk.

Saw dust

Saw dust, an abundant agro waste was explored for the removal of metal ions and dyes. Saw dust from different sources have been researched for their capability to act as an adsorbent. Vaishya and Prasad[6] researched on the removal of Cu^{2+} ions by saw dust. Ajmal et al[7] investigated the phosphate treated saw dust from mango tree as potential sorbent for the removal of Cr^{6+} ions from electroplating effluents. The pretreated saw dust was found to show 100% removal efficiency for Cr^{6+} ions from industrial effluents. Ferrero[8] reported the use of saw dust from various sources for the removal of polar blue and methylene blue from aqueous solution. Saw dust from walnut shoed highest loading capacity of polar blue and methylene blue compared to other saw dust in the report. Malik[9] investigated the use of carbon from saw dust as a potential adsorbent for the removal of metanil yellow and loading capacity was found to be 183.6 mg g^{-1}. Saw dust from neem source was explored for the removal of methylene blue and malachite green by Khattri and Singh[10].

Coir pith

Namasivayam and Kadirvelu[11,12] investigated the use of coirpith as low cost adsorbent for the removal of Hg^{2+}, Ni^{2+} and Cu^{2+} ions. The coirpith waste was pretreated with sulfuric acid and ammonium persulphate prior to the adsorption studies. Namasivayam and Sangeetha[13] reported the use of $ZnCl_2$ as activating agent for coirpith and the removal efficiency was found to be very high compared to untreated coirpith. The increased efficiency was found to be due to high surface area of coirpith after activation. Namasivayam et al[14,15] reported the use of coirpith raw and activated for the removal of acid brilliant blue, rhodamine B and acid violet. It was observed that with activation the loading capacity increased and rate of adsorption was found to be spontaneous.

Sugarcane bagasse

Sugarcane bagasses abundant by product obtained from sugar industries are found to have 50% cellulose, 27% ployoses and 23% lignin. These biopolymers make sugarcane bagasse a rich adsorbent with variety of functional groups. Khattri and Singh[16] explored the possibilities of sugarcane dust as low cost adsorbent for the removal of crystal violet, rhodamine B and methylene blue form aqueous solution. The loading capacity of sugarcane dust was found to be low compared to other agro based sorbents. In case of heavy metal ions, sugarcane bagasse was pretreated with many activating agents and studied for the removal of heavy metal ions such as Cu^{2+}, Cd^{2+} and Pb^{2+} ions.

Peanut shell

Peanut shell, a mass agricultural waste was evaluated in raw, pretreated and activated carbon forms for the removal of heavy metal ions. Wilson et al[17] and Romero et al[18] reported peanut shell based activated carbon for the removal of various heavy metal ions. Chamarthy et al[19] reported the use of activated peanut shell for the removal of five heavy metal ions and found that the efficiency was higher than many commercial adsorbents. Kannan and Sundaram[20] studied the use of peanut shell carbon for the removal of methylene blue along with rice and coconut shell carbons. The peanut shell showed lowest loading capacity compared to rice and coconut shells. Malik et al[21] reported the removal of malchanite green by activated carbon from peanut shell and found to be effective.

Fruit/Vegetable waste based adsorbents

Orange peels

In 1996, Namasivayam et al[22] explored the use of orange peel waste for the removal of dyes such as cango red, procion orange and rhodamine B from aqueous solution. The equilibrium data were found to fit well with Langmuir and Freundlich isotherms. Since then many researchers started exploring the use of orange peel for the removal of heavy metal ions and dyes with several modifications. In 2001, Rajeshwari et al[23] reported the removal of acid violet 17 by orange peel from aqueous solution. The loading capacity was found to be high at pH 2 and a maximum of 60% of desorption was obtained at pH 10. Annadurai et al[24] studied the removal of five dyes such as methylene blue, crystal violet, rhodamine, congo red and methyl violet using orange peel as cellulose based adsorbent. The equilibrium data for all dyes was found to obey both Langmuir and Freundlich isotherm in the concentration range of 10-120mg L^{-1}. An alkaline pH was found to be favorable for the removal of all dyes.

Annadurai et al[25] reported the use of orange peel and banana peel for the removal of heavy metal ions from aqueous solution. In 2008, Li et al[26] reported the removal of Cd^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} ions by orange peel modified with various bases (NaOH, NH_4OH and $Ca(OH)_2$) and with acids ($C_6H_6O_7.H_2O$, $H_2C_2O_4$ and H_3PO_4). The loading capacity of Ni^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+} ions was found to be increased by 95, 175, 60 and 130%. Schiewer and Balaria[27] investigated the native and protonated orange peel for the removal of Pb^{2+} ions from aqueous solution. The results were found that protonated orange peels have shown highest loading capacity compared to native peels. This is due to the elimination of alkali and alkaline earth metal ions present in the native orange peels. FTIR studies of protonated orange peels after adsorption of Pb^{2+} ions suggested that hydroxyl and carboxyl groups are major contributors in metal uptake. Ning-Chuan et al[28] studied the removal of Cu^{2+} ions by orange peel chemically modified with sodium hydroxide and calcium chloride. The modified adsorbent was successfully regenerated with HCl for five times with little loss in loading capacity. Liang et al[29] successfully demonstrated K^+ type and Mg^{2+} type orange peel for the removal of Cu^{2+} ions from aqueous solution and K^+ type orange peel showed the highest loading capacity compared to Mg^{2+} type adsorbent.

Adsorption of Pb^{2+} and Zn^{2+} ions from aqueous solution onto sulfured orange peel was studied by Liang et al[30]. The removal of hexavalent chromium by iron nanoparticle embedded orange peel pith from aqueous solution was examined by Lopez-Tellez et al[31]. The loading capacity of iron nanoparticle incorporated orange peel was found to be twice than the unmodified orange peel. Ningchuan et al[32] reported the grafted copolymerization of orange peel and its application towards the removal of Pb^{2+}, Cd^{2+} and Ni^{2+} ions from aqueous solution. The loading capacity was found to be 476.1, 293.3 and 162.6 mg g^{-1} respectively or Pb^{2+}, Cd^{2+} and Ni^{2+} ions. FTIR study demonstrated that the hydroxyl and carboxyl groups were involved in the biosorption of metal ions.

Banana peels

Banana peel waste from banana fruit was found to have the properties of binding heavy metal ions and synthetic dyes from water. Annadurai et al[24] reported the removal of five dyes such as methylene blue, crystal violet, rhodamine, congo red and methyl violet using banana peel as cellulose based low cost adsorbent along with the orange peel. Comparatively banana peel was found to have the highest loading capacity compared to orange peel for all the dyes. After identifying the ability of banana peel to remove synthetic dyes; Annadurai et al[25] studied the removal of heavy metal ions by banana peel from aqueous solution. The loading capacity of banana peel towards heavy metal ions was found to be higher than orange peel. Following this, several researchers have studied the removal of heavy metal ions from aqueous solution by banana peel [33-35]. In 2009, Achak et al[36] investigated the adsorption of phenolic compounds from oilve mill waste water. The adsorption was found to increase with increase in dose of banana peel and with pH. The experimental data obtained were found to fit well with both Freundlich and Langmuir isotherms.

Amel et al[37] investigated the use of raw and activated banana peel for the removal of cationic dye such as methylene blue from aqueous solution. The loading capacity of activated banana peel was found to be high compared to the natural banana peel. The higher loading capacity of activated banana peel is due to the increase in surface area and porosity of the banana peel during activation with caustic soda. Very recently, Mohammed and Chong[38] explored the use of banana peel as the novel and potential adsorbent in the treatment and discolourizaion of biologically treated palm oil mill effluent. The study was executed with three different forms of banana peel such as natural, methylated and activated carbon. It was found that significant removal of color, total suspended solids (TSS), chemical oxygen demand (COD), biological oxygen demand (BOD), tannin and lignin was observed by banana peel activated carbon. These results suggest that the banana peel is an effective adsorbent for the removal of heavy metal ions, dyes, phenols, tannins and lignin.

Mango peels

Mango occupies 5th rank in productions among the major fruit crops. Mango peel and kernel are considered as waste due to no commercial value. Mango seed kernel powder was studied as adsorbent for the removal of methylene blue from aqueous solution[39]. The process was found to follow pseudo first order and controlled by both surface and pore diffusion. Davila-Jimenez et al[40] performed the adsorption of anthraquinone and azo acid dyes from aqueous solution by husk of mango seed and two carbonaceous materials as adsorbent. The three adsorbents were used for the removal of eight acid dyes such as acid blue 80 and 324, acid green 25 and 27, acid orange 7.8 and 10 and acid red 1 from aqueous solution. It was observed that the adsorption of eight dyes onto three prepared mango seed kernel adsorbents was due to binding onto surface active sites.

Iqbal et al[41,42] explored the possibilities of removal of Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} ions from aqueous solution by native mango peel. A study was executed by chemically modifying the mango peel to know the functional groups involved in uptake of Pb^{2+} and Cd^{2+} ions. The results showed that 76.26 and 72.46% of the removal of Pb^{2+} and Cd^{2+} ions was due to the carboxylic groups and 23.74 and 26.64% was due to the hydroxyl groups suggesting that the carboxylic groups of native mango peel are predominant contributors in uptake of Pb^{2+} and Cd^{2+} ions from aqueous solution. The release of cations from mango peel during adsorption of Pb^{2+} and Cd^{2+} ions and EDX patterns suggested that the mechanism of adsorption is ion exchange. Regeneration of native mango peel was successfully attained for five cycles without any loss in the loading capacity.

Pomegranate peels

Pomegranate peel was used as potential adsorbent for the removal of Pb^{2+} and Cu^{2+} ions from aqueous solution[43]. The study was carried out with raw, two forms of chemically activated and activated carbon from pomegranate peels. Batch studies were carried out and found that the pH 5.6 and 5.8 was optimal for the removal of Pb^{2+} and Cu^{2+} ions from aqueous solution. Amin[44] explored the use of different activated carbon prepared from pomegranate peel for the removal of direct blue-106 dye from aqueous solution. The adsorption was found to be high at pH 2 and follows pseudo second order kinetic model. Adsorption of 2, 4-dichlorophenol from aqueous solution by the pomegranate peel was investigated by Bhatnagar and Minocha[45]. Batch and column studies were carried out to access the potential of pomegranate peel. The removal of Ni^{2+} ions from aqueous solution by the pomegranate peel was investigated by Bhatnagar and Minocha[46]. Ay et al[47] characterized the pomegranate peel with BET, FTIR, TG and zeta potential analyzer and studied its adsorption behavior towards Pb^{2+} ions and acid blue 40 dyes from aqueous solution. The loading capacity of pomegranate peel was found to be high for Pb^{2+} ions and acid blue 40.

Jackfruit peels

Jackfruit peel rich in lignin was explored as adsorbent for the removal of Cd^{2+} ions from aqueous solution[48]. Prior to adsorption studies, jackfruit peel was pretreated with sulphuric acid for carbonization. Batch experiments were performed and the kinetic and equilibrium data was studied with various kinetic and isotherm models. Hameed[49] reported the use of raw jackfruit peel for the removal of methylene blue from aqueous solution. The removal of MB was found to constant from pH 4-10 and decreased beyond pH 10. The results demonstrated the effectiveness of jackfruit peel as potential adsorbent for the removal of cationic dyes from aqueous solution.

Grape peels

Grape peels were explored as low cost adsorbent for the removal of Cd^{2+} and Ni^{2+} ions from aqueous solution by batch technique[50]. The recovery % of Cd^{2+} and Ni^{2+} ions from adsorbed grape peels was more than 97% with 0.1HCl solution. Saeed et al[51] carried out batch mode adsorption studies for the removal of crystal violet from aqueous solution by grape peels. The adsorption was found to be rapid and 97% of crystal violet was removed with in 60min. A 98% of adsorbed dye was able to recover from grape peels using 0.1M NaOH solution. The results suggested that grape peels can be potential adsorbent for the removal of heavy metal ions and dyes from aqueous solution.

Watermelon rind

Watermelon rind yet another agricultural by-product which is abundantly available during summer season is explored as low cost adsorbent for the removal of heavy metal ions and synthetic dyes. Lakshmipathy et al[52,53] and Anvesh et al[54] reported the removal of heavy metal ions such as Cd^{2+}, Ni^{2+}, Co^{2+} and Cr^{3+} from aqueous solution. Similarly, the removal of cationic synthetic dyes such as methylene blue, crystal violet and rhodamine B was carried out with protonated watermelon rind and it was found that MB showed highest adsorption capacity compared to CV and RB[55]. In another study, native and acid activated watermelon rind was compared for the removal of Brilliant green from aqueous solution and it was reported that acid activated watermelon rind showed highest loading capacity[56]. Recently, the removal of Pb^{2+} ions from aqueous solution was studied in continuous column mode and found that the removal efficiency is better than many other commercial adsorbents[57]. It was observed that acid treatment of watermelon rind enhanced its sorption capacity towards cations.

Conclusion

The literature review revealed that many fruit peels and seeds are investigated and reported as low cost adsorbents for the removal of heavy metal ions, synthetic dyes and organic contaminants from waste water. Most of the studies were carried out in batch process and very few adsorbents were studied in continuous column studies. It was observed that the chemical activation or modification of adsorbents increases the removal efficiency and the loading capacities. However, the loading capacity of adsorbents without any pretreatments was found to be low and the treatment techniques few employed were costlier limiting its application. Hence, low cost, easily and abundantly available adsorbents are still in need for the effective removal of organic and inorganic contaminants from waste water.

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