Plant Archives Vol. 23, No. 2, 2023 pp.491-500 e-ISSN:2581-6063 (online), ISSN:0972-5210

Plant Archives

Journal homepage: http://www.plantarchives.org
DOI Url : https://doi.org/10.51470/PLANTARCHIVES.2023.v23.no2.078

TREATING WASTEWATER THROUGH ADSORPTION PROCESS BY USING AGRICULTURAL WASTE: A REVIEW

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(Date of Receiving : 12-07-2023; Date of Acceptance : 30-09-2023)

ABSTRACT

The scarcity of water due to economic and population growth is considered as a huge challenge for the human kind. Therefore water treatment technologies are required for the sustainable future. The available reverse osmosis system has not enough to solve the problem as this process uses lots of ground water in water treatment. Therefore, the current need of our society is to get an alternate way which is environmentally secure, recyclable and reusable, cost-effective and also have the capability to solve the potential problems of our society. For this purpose, adsorption is known to be one of the best techniques applied for the wastewater treatment because it is cost-effective, economical and eco-friendly. Most of the sorbents such as agricultural waste materials are used for the removal of heavy metals from wastewater. These materials are abundant in nature, environment friendly, reusable and low in cost. This article focuses on reviewing the recent progress in the application of various agricultural waste materials for the wastewater treatment. The literature survey here is concentrated on the outcomes of the various agricultural waste materials which have been actively used in recent years such as- papaya seed, egg shell, coconut leaf powder, rice husk and rice straw, potato peels, orange peels, saw dust and maize cob and husk etc.
Keywords **:** Adsorption process, Low-cost adsorbents, Wastewater treatment, Sustainable technologies, agricultural wastes

1. Introduction

In recent years the quality of water degraded continuously because of population burst, anthropogenic activities, rapid urbanization and industrialization and excessive use of natural water resources. The increasing awareness regarding the importance of natural water resources has pushed the researchers towards the development of robust, economically feasible and environment friendly technique which capable enough to eliminate the pollutants from water and also to safeguard the health of affected population (Renge *et al.,* 2012). There are various treatment technologies available with different degree of success to control and minimize water pollution. Various shortcomings are related with technologies such as high operational and maintenance costs, generation of toxic byproducts and complicated procedure involved in the treatment of water. Therefore, comparatively adsorption process is a better alternative for waste water treatment because of its convenience, easily operational and of simple design in wastewater treatment plants adsorption processes are applied for the removal of dissolved pollutants which remain after chemical oxidation treatments. The most commonly used adsorbents are the activated carbon based adsorbents. These are commonly used for the removal of organic compounds and heavy metals from wastewater. But this is costly process. Hence, low-cost adsorbents are have been used and categorized into following groups such as- agricultural waste, household waste, industrial by products, sludge, sea materials, soil and ore materials and novel low-cost adsorbents (Bhatnagar *et al.,* 2015). Low-cost adsorbents are known for their ability to remove various types of pollutants from wastewater. Hence, switching from activated carbon adsorbents to low-cost adsorbents such as by products generated from agricultural activity and industry are cost-effective and also solve the problem of disposal of the agricultural waste i.e. rice husk, petroleum waste, scrap tires, etc. All these are utilized to reduce the pollution of wastewater (Ali *et al.,* 2012).

Over the last few decades, the low-cost adsorbents had been used to treat water and wastewater. Thus, the aim of the study is to review the current literature based on the application of low-cost adsorbents used for the treatment of wastewater (Ungureanu *et al.,* 2015).

The discussion includes the affinity of adsorbents in removing various types of pollutants, natural effect, cost-effective, ad its usability after cleaning process.

This article is structured as the information regarding adsorption processes which is reported in section 2, the low-cost agriculture based adsorbents and their capacities of pollutant removal from wastewater are mentioned in section 3, table 1. Section 4 and 5 includes the further discussion and conclusion respectively.

2. Adsorption Mechanism

Adsorption is the most profitable process and more efficient than the conventional methods. This process is one of the greatest technologies applied for the wastewater treatment because it is an effective, economical and eco-friendly treatment technique. Adsorption is mainly a mass transfer way by which the metal ions are transferred from the water to the surface of sorbents, and attached with the physical or chemical interactions. The substances which are adsorbed known as the adsorbate and the material on the surface of which they attach is known as adsorbent. The functional groups attached with adsorbents play an important role in determining the effectiveness, capacity, and reusability of these adsorbents (Yagub *et al.,* 2014). Generally, adsorption involves interaction between pollutants and adsorbents in the following steps such as-

1. Attaching of the metal ion from the water to the surface of the adsorbent.
2. Transfer of the metal ion by pore diffusion from outer surface of adsorbent to the inner surface of porous structure based adsorbents.
3. Adsorption of heavy metal ions onto the active sites of the adsorbent.
4. The rate of adsorption is determined by either film formation or intra particle diffusion.

If the interaction between the adsorbents and the adsorbed metal ions is of physical nature, the process is known as physisorption. The Vander Waals weak forces are involved among them and the process is reversible and occur at critical temperature of the adsorbed substance. Whereas, if the adsorbates are attached on the adsorbents surface with chemical bonding, the adsorption process is known as chemisorption. This process is irreversible in nature because adsorbates chemisorbed on adsorbents are hard enough to remove from the surface of the adsorbents because of stronger forces at stake. Both the processes can occur simultaneously or alternatively, in favorable environment. Physical adsorption process is exothermic in nature because it is accompanied by a decrease in free energy and entropy of the adsorption system. In a solid–liquid adsorption system, the solutes have been removed from the solution by the accumulation of solutes at solid surface. The remaining solute in the solution attains a dynamic equilibrium with that one which are adsorbed on the solid surface. The amount of adsorbate which has been taken up by an adsorbent as a function of both temperature and concentration of adsorbate, can be determined by an adsorption isotherm according to the general equation:

$$q_t = (C_0 - C_t).V/m$$

Where q_t (mg/g) is the amount of adsorbate per unit mass of adsorbent at time t, C_0 and C_t (mg/l) is theconcentration of adsorbate at initial and after time t, respectively, V is the volume of the solution (in liter), and m is the mass of adsorbent (g) (Coonery, 1999). For the removal of a wide range of contaminants from industrial and municipal waste waters, landfill leachate and contaminated groundwater, the most effective media i.e. activated carbon is widely used. Carbon is being used to treat Different contaminants and maintain the total flow. It is better utilized for the removal of specific contaminants. The activated carbon is produced from various natural raw materials so, it inhibits different properties. Apart from the raw material, the coal can also be used as activated carbon source by employing the particular activation process of physical nature. The process is completed by contact of coal with a high temperature steam flow (800– 1000 °C). Activation process can be done by chemically too with the use of acids.On the basis of bulk density, several activated carbon classes can be identified such as, the macroporous carbon, mesoporous carbon and the microporous carbon. The bulk densities of macroporous carbons, mesoporous carbons and the microporous carbons are more than 1 cm^3/g (pore space volume for gram of carbon), in the range 0.85–1.0 cm^3/g and less than 0.85 cm^3 /g. For the removal of large contaminants, macroporous and mesoporous carbons are used whereas for the removal of small contaminants microporous carbons are more suitable (Tchobanoglous *et al.,* 2003).The content of ash, raw material used, number of regeneration cycles, specific surface area and the Iodine number defines the efficient properties of activated carbons. For activated carbons, the content of ash is less than 15%. Basically, ash content value increases with the number of regeneration cycles, by the percentage value of 0.5% to 1.0% after each cycle. This imposes limitation on the number of possible regenerations. Adsorption capacities increase with the increase of an important parameter i.e. specific surface area and expressed in m^2 /g. For activated carbons, the specific surface area lies in the range of 500 to 1500 m^2 /g.The Iodine number defines the ability of the adsorbent to adsorb small contaminants, represents as mg of iodine adsorbed per gram of carbon. The Iodine number for activated carbon is lies in the range of 500–1200 mg/g Bonomo, 2008.

3. Low-Cost Adsorbents

Most adsorbents applied for the removal of heavy metals from wastewater are derived from either modified natural polymers or agricultural waste materials. These materials are abundant, environmentally friendly, reusable and of low in cost.

3.1. Agricultural waste

The agricultural solid wastes coming from natural resources such as agave bagasse (Juang *et al.,* 2002), almond shell (Aygun *et al.,* 2003), apricot shell (Aygun *et al.,* 2003), barley straw (Pehlivan *et al.,* 2012), cashew nutshell (Kumar *et al.,* 2011), citric acid (Pehlivan *et al.,* 2012), corncob (Juang *et al.,* 2002), cotton and gingelly seed shell (Thinakaran *et al.,* 2008), depectinated pomelo peel (Tasaso, 2014), Egyptian mandarin peel (Husein, 2013), fruit juice residue (Yadav *et al.,* 2015), garden grass (Hossain *et al.,* 2012), garlic peel (Liu *et al.,* 2014), grapefruit peel (Zou *et al.,* 2012), hazelnut-shell (Aygun *et al.,* 2003), mango peel (Iqbal *et al.,* 2009), Mosambi peel (Saha *et al.,* 2013), pine sawdust (Akmil-Basar *et al.,* 2005), lentil-shell powder (Aydın *et al.,* 2008), pongam seed shell (Thinakaran *et al.,* 2008), musk-melon peel (Huang *et al.,* 2013), groundnut-shell (Malik *et al.,* 2007), olive stone powder (Fiol *et al.,* 2006), plum waste material(Juang *et al.,* 2002), pomegranate peel (Moghadam *et al.,* 2013), pomelo peel (Tasaso, 2014), potato peel (Aman *et al.,* 2008), rice shell (Aydın *et al.,* 2008), rice straw (Ding *et al.,* 2012), sugarcane bagasse (Khoramzadeh *et al.,* 2013), walnut-shell (Aygun *et al.,* 2003), banana peel (Annadurai *et al.,* 2002), cane pith (Juang *et al.,* 2001), coir pith (Namasivayam *et al.,* 2001), yellow passion fruit (Pavan *et al.,* 2008), orange peel (Liang *et al.,* 2011), rice husk (Ding *et al.,* 2014), sawdust carbon (Malik, 2003), soy-meal residue (Arami *et al.,* 2006), sunflower stem (Sun and Xu, 1997), ash (Chou *et al.,* 2001), white rice-husk (Tavlieva e al. 2013), wood based biochar material (Kizito *et al.,* 2015), sky fruit husk (Njoku *et al.,* 2014), pomegranate peel (Bhatnagar *et al.,* 2010), biomass material (Euphorbia rigida) (Gercel *et al.,* 2008), pine-wood powder (Tseng *et al.,* 2003), almond shells powder (Doulati Ardejani *et al.,* 2008), ash gourd peel (Sreenivas *et al.,* 2014), cucumis-sativa peel (Pandey *et al.,* 2014), lentil husk (Basu *et al.,* 2015), neem tree bark (Maheshwari *et al.,* 2015), sunflower pod (Witek-Krowiak, 2012), wheat stalk (Tan *et al.,* 2009), carbon based cloth materail (Ayranci and Hoda, 2004), cassava peel (Owamah, 2014), and coconut-shells (Pillai *et al.,* 2014) have been actively used for the removal of various dyes from aqueous solutions. The main functional group components of the agricultural waste materials include hemicelluloses, lignin, lipids, proteins, simple sugars, water, hydrocarbons and starch, having a potential sorption capacity for various pollutants (Bhatnagar *et al.,* 2010). Agricultural waste products are used in both the way natural and modified. In the natural form, the product is washed, made fine paste until it attains the desired particle size and after that used it as adsorbents in adsorption process for the treatment of wastewater. Whereas, in the modification of agricultural waste, the agricultural waste is pre-treated by modification techniques (Bhatnagar *et al.,* 2010). This modification of agricultural waste enhances the functional group capacity of cleaning and also increases the number of active sites on the surface of adsorbents. Agricultural waste materials have been widely tested for the adsorption process for the removal of pollutants from the aqueous solution. The most significant examples are mentioned here in which agricultural waste materials are used as sorbents for the removal of dyes from aqueous solution. Aygun *et al.,* 2003, used almond shell, hazelnut-shell, walnut-shell and apricot stone as raw materials and modified agricultural waste as granular activated carbon (GAC). GACs are known for their physical properties such as attrition, bulk density, etc. chemical properties such as elemental composition, % weight loss, etc., morphological properties such as surface area, surface chemistry, etc., and adsorption properties such as iodine number, phenol and methylene blue adsorption.GAC formation is independent of elemental composition but depends on type of formation. With pyrolysis temperature and activation time with $ZnCl_2$, the adsorption capacity of prepared GACs have been increased which shows the following order of raw materials usability for the methylene blue adsorption especially for the GACs formed from hazelnut and walnut-shells as- hazelnut-shell > walnut-shell ~ apricot stone > almond-shell. Juang *et al.,* 2002, prepared the activated carbon sample from bagasses by steaming the carbons at different extents of burn off by varying the temperature in the range of 750–840 °C. The prepared carbons then ground in a mill to make a fine paste after that washed and dried it. This will increase the volume fraction of mesopores and micropores from 22.3 to 31.1% with increasing the extent of burn-off from 80.6 to 91.3 wt%. The iodine number of the prepared carbons, as well as the adsorption capacities have also increased. The adsorption capacity has tested for the removal of two commercial dyes Acid blue 25(AB 25) and Basic red 22(BR 22) from water which resulted increase with the increase in the extent of burn-off. Thinkaran *et al.,* 2008, used gingelly (sesame) (S), cotton (C) and pongam (P) seed shells and prepared activated carbons and used the prepared sample for the removal of Acid Red 114 (AR 114) from water. The synthesis of activated carbons from raw materials involves the repeatedly washing of raw materials with distilled water to remove dust and other impurities, followed by drying of raw materials in the sunlight for 48 hrs, after that cutting of these into small pieces and soaked in sulphuric acid (1:2, W/V) and heating the sample for 24 hrs at 80^0C in a muffle furnace. After the chemical treatment all the samples of different raw materials have holed to room temperature and washed several times until the pH gets neutral. The washed samples then dried in hot air oven at 105^0C. After this process prepare a fine power. W the treated powder samples of activated carbons have used for the removal of AR114. The results showed the higher removal percentages at lower concentration of AR114 ~ 3g/L. The removal efficiencies of the adsorbents are in the order of S < C < P. Akmil-Başar *et al.,* 2005, studied the removal of malachite green (MG) dye from aqueous solutions using two different adsorbents (CZn5, PETNa8), prepared from pine sawdust and polyethyleneterephatalate (PET) by chemical activation with $ZnCl_2$ and NaOH, respectively. The study has based on dye concentration, pH and contact time to test the adsorption capacity of adsorbents. Both adsorbents CZN5 and PETNa8 have effectively removed the dye at higher concentration, at favorable pH range 6-10 with equilibrium times as 120 min and 90 min respectively, having order of adsorption capacities are as CZn5 > PETNa8.Malik *et al.,* 2007, used ground-nutshell for the preparation of an adsorbent by chemical activation using $ZnCl_2$ under optimized conditions. The comparative study has also been done between the characteristics of novel activated carbon and commercially available powdered activated carbon (CPAC). The surface area, iodine and methylene blue number of novel activated carbon is higher than CPAC. The study used both the carbon samples for the removal of MG dye from water by using dye concentration (100–200 mg/l), adsorbent concentration (0.1–1 g/l) and duration of cleaning (5–120 min). The novel activated carbon sample showed 94.5% removal of the dye in 30 min for the adsorbent concentration of 0.5 g/l and dye concentration of 100 mg/l, whereas CPAC showed 96% removal of the dye in 15 min for the similar composition of experiment. Tseng *et al.,* 2003, studied the Physical properties of activated carbons prepared from pinewood at different activation times (0.5, 1.5, 2.7, and 4.0 h) in steam at 900 °C, followed by grinding in a mill and washing with water, drying and sieved in the size range 0.12–0.20 nm. Prepared pinewood-products have been used for the removal of three dyes Acid blue 264 (AB 264), Basic blue 69 (BB 69), Methylene blue (MB) from aqueous solutions at 30 °C. The adsorption capacities of the adsorbents are in the order of AB 264 > BB 69 > MB. Annadurai *et al.,* 2002, used banana and orange peels as adsorbents to study the removal of dyes such as methyl orange (MO), methylene blue (MB), Rhodamine B (RB), Congo red (CR), methyl violet (MV), amido black 10B (AB). The peels are dried, grinded, and washed thoroughly with deionized water to remove dirt and dust, followed by drying in an air oven at 100–120 °C for 24 h. After drying, the treated sample is sieved through a 5 mm mesh size. The adsorption capacities of the treated samples have decreased in the order of methyl orange (MO) > methylene blue (MB) > Rhodamine > (RB) > Congo red (CR) > methyl violet (MV)

> amido black 10B (AB) in the removal process of dyes. Pavan *et al.,* 2008, used yellow passion fruit (YPFW), a powdered solid waste, as bio-sorbent for the removal of Methylene blue (MB). The powdered solid waste is washed several times with distilled water and dried in the sunlight for 48 h. after grind the final material and sieved with the particle size less than 250 µm and subsequently washed the powder with doubly distilled water for 10 min and dried in an oven at 60 °C temperature for 24 hours. Now prepared powdered material has preserved in the desiccator for further use in the adsorption studies. The adsorption efficiency has test of the prepared powder sample in the removal of MB dye at room temperature. The adsorption of MB dye is favorable in the basic pH range for 48 hrs of contact time and is 44.67 mg/g. Malik, 2003, used mahogany sawdust and rice husk and prepared activated carbons and studied it as adsorbents for the removal of Acid Yellow 36 [AY 36]. The adsorption capacities of both the activated carbons prepared from sawdust and rice husk are 183.8 mg/g and 86.9 mg/g for the pH value of 3, respectively. Arami *et al.,* 2006, used soy meal hull (SMH) for the removal of four textile dyes, Direct red 80 (DR80), Direct red 81 (DR81), Acid blue 92 (AB92) and Acid red 14 (AR14) from an aqueous solution. The adsorption is favorable for the pH value of 2 and adsorption capacities of SMH for the for dyes removal are 178.57, 120.48, 114.94 and 109.89 mg/g of adsorbent, respectively. Hence, based on results, author concluded that SMH is a natural, eco-friendly and low-cost adsorbent with relatively large adsorption capacity suitable for the removal of dyes from aqueous solutions. Ezechi *et al.,* 2015, used Ageratum conyzoides leaf powder, collected in a rural area of Malaysia, to test the adsorption capacity for the removal of MB dye. The collected leaves have washed several times with distilled water to remove surface dust particles and dried it in the sunlight for 48 hrs, followed by drying in the oven at 60 °C temperature for 24 hours. The dried leaves have been grinded and sieved to particle size of 75–100 µm. After washing the prepared powder by 15 times to remove chlorophyll pigments and again dry the prepared sample in the oven at 60 °C for 24 h stored in a container for further use of adsorption study. The better results are found at pH value of 4 which is the 91% removal of MB dye after 20 min of adsorption process with the initial concentration of 20 mg/l. Gürses *et al.,* 2014, used Aşkale lignite for the removal of MB dye from aqueous solution. In this experiment the waste adsorbent is not treated and also study the effect of temperature, dye concentration, pH and ionic strength on the adsorption capacity of the Aşkale lignite waste. They fixed the contact time of 20 min, adsorbent amount of 0.15 g, temperature f reaction of 20°C, neutral pH value and varied the adsorbate concentration of 10, 20, 40, 60, 80 and 100 mg/l and analyzed that the adsorption capacity increases with increase of concentration of adsorbate as about 7 mg/g, 13 mg/g, 22.5 mg/g, 26 mg/g, 29 mg/g and 32 mg/g, respectively. Shi *et al.,* 1999, have tested the adsorption capacity of sunflower stalks by chemically grafting quaternary ammonium groups on them. They studied the adsorption capacity of the prepared samples in the removal of Congo red (CR) and direct blues (DB) dyes with the chemically modified and raw sunflower samples. The maximum adsorption capacities are obtained for modified sunflower stem powder sample as compared with the raw ones, which is to be 191 and 216 mg/g for CR and DB respectively.Tavlieva *et al.,* 2013, used white rice husk as adsorbent for the removal of brilliant green (BG) in aqueous solutions. The maximum adsorbent capacity is found to be 85.56 mg/g at the temperature of 47 °C with a contact time of 60 min. when they changed the adsorbate concentration of 3, 6, 8, 20, 40 and 100 mg/l the adsorbent capacity changes as about 0.8 mg/g, 0.9 mg/g, 1.0 mg/g, 3.0 mg/g, 7.0 mg/g and 18 mg/g, respectively with the adsorbent concentration of 5 g/l and contact time of 60 min. They have concluded that the increase in temperature is favorable for BG adsorption and fast adsorption take place at 47 °C. Ding *et al.,* 2014, studied the removal of Rhodamine-B (RhB) by using treated rice husk-based activated carbon. The process of treatment involves the mixing of rice husk with phosphoric acid in a mass ratio of rice husk to phosphoric acid of 1:4, followed by heating upto 500 °C for 1 hr. The obtained powder is treated with various ways and prepared different samples. In the first way the obtained powder is just washed until to get neutral pH and named as P-AC. The second way is that the obtained powder is washed with the hot water (95 °C) until to get neutral pH and named the sample as P95-AC.In the third way, the obtained powder sample is washed with the distilled water until to get neutral pH and mixed into 3 wt% potassium hydroxide solution. The mixture is allowed to boil under reflux condition for 1 hr. after filtering the mixture the solid obtained product has named as PK-AC. Another treatment of raw rice husk for the production of activated carbon has mentioned by author such as taking the mixture solution of mass ratios of rice husk to KOH was 1:4, and carried the reaction at 400 °C for half an hour and then 800 °C for 1 h. Thus, prepared activated carbon sample is named as K-AC. Results shows that PK-AC is an effective adsorbent for removal of RhB from aqueous solution and reaction is dependent on the Initial RhB concentration and temperature and less affected from pH.

The use of agriculture waste adsorbent materials for the removal of heavy metals from single compound aqueous solution are herein described such as Ligno-cellulosic and Agave bagasse materials. Ligno-cellulosic exhibits a very complex structure which contains a variety of active sites that are capable enough for adsorbing contaminants from aqueous solutions, whereas, Agave bagasse is a sub-product of alcohol industry which has been very little studied, which could have the potential to remove a variety of contaminants from aqueous solutions.

Pandey *et al.,* 2014, have used chemically modified cucumis-sativus peels (CSP), treated with HCl in the removal of Cd (II) ions from aqueous solutions. The removal efficiency was 84.85% for the initial concentration of 20 mg/l of Cd (II) ion at pH value of 5 and also studied the adsorption isotherms for the metal ion concentrations ranging from 5 to 150 mg/l. Sreenivas *et al.,* 2014, used ash gourd peel for the removal of chromium (VI) metal ions. Treatment process involves the grinding and sieving to get particle size (446 µm). The result showed more than 91% of Cr (VI) ions gets adsorbed on the surface of ash gourd peel powder with the initial adsorbent concentration of 6 g/l used for the removal of initial Cr (VI) ions concentration of 125 mg/l in an aqueous solution, which gives the adsorption capacity of ash gourd peel powder as the value of 18.7 mg/g.

Table 1 : Agricultural waste based adsorbent material, pollutants removed, contact time along with their adsorption capacities

S. No.	Agricultural waste as adsorbents	Pollutants	Contact time/pH/ temperature	Maximum removal	Refs.
1	Saw dust	Cr (IV), Pb (II)	-	-	(Ahmad *et al.,* 2004)
2	Activated carbon from almond-shell	Methylene blue	24 hrs.	1.33 mg/g	(Aygun *et al.,* 2003)
3	Activated carbon from orange peels	Cd, Cu, Pb, Ni	-	-	(Lasheen *et al.,* 2012)
4	Activated carbon from rice husk and rice straw	Pb, Cr, Cu, Ni	-	-	(Nhapi *et al.,* 2011)
5	Casava peels based Activated carbon	Pb, Cu	120 min.	5.8 mg/g; 8.0 mg/g	(Owamah, 2014)
6	Raw and modified activated carbon of agave bagasse by HCl, HNO_3 & NaOH	Cd, Pb, Zn	-	13.27 mg/g, 12.50 mg/g, 13.50 mg/g, 18.32 mg/g; 35.60 mg/g, 42.31 mg/g, 54.29 mg/g, 50.12 mg/g; 7.84 mg/g, 12.40 mg/g, 14.43 mg/g, 20.54 mg/g	(Velazquez-Jimenez *et al.,* 2013)
7	Raw grass	Pb	-	58.34 mg/g	(Hossain *et al.,* 2012)
8	Banana Peel based activated carbon	Cd, Pb	20 min.	5.71 mg/g; 2.18 mg/g	(Anwar *et al.,* 2010)
9	Raw and modified Egyptian mandarin peel	Hg	24 hrs.	19.01 mg/g, 34.84 mg/g, 23.26 mg/g	(Husein, 2013)
10	Cashew nutshell powder	Ni	30 min.	18.86 mg/g	(Kumar *et al.,* 2011)
11	Ash gourd peel	Cr	60 min.	18.7 mg/g	(Sreenivas *et al.,* 2014)
12	Maize cob and husks	Zn, Cd, Pb	-	-	(Igwe *et al.,* 2005)
13	Chemically treated Potato peels	Pb, Cd, Zn	-	-	(Taha *et al.,* 2011)
14	Pomelo peel	Cu	60 min.	19.7 mg/g	(Tasaso, 2014)
15	Raw and citric acid modified barley straw	Cu	120 min.	31.71 mg/g	(Pehlivan *et al.,* 2012)
16	Bio-char	Ammonium nitrogen	20 hrs.	39.8 mg/g, 44.64 mg/g	(Kizito *et al.,* 2015)
17	Rice husk powder	Phenol,1,3-Dihydoxybenzene	60 min.	1.53×10^{-4} mol/g; 8.07×10^{-5} mol/g	(Mbui *et al.,* 2002)
18	Rice husk	Phosphate	180 min.	97.0%	(Yadav *et al.,* 2015)
19	Activated carbon from coconut-shells	Urea	200 min.	60 mg/g; 256.41 mg/g	(Pillai *et al.,* 2014)
20	Raw and activated form of fruits residue	Phosphate	180 min.	99.9%	(Yadav *et al.,* 2015)
21	Activated carbon from pomegranates tree woods	Anionic herbicide bentazon	10 hrs.	80.0 mg/g	(Salman *et al.,* 2013)
22	Activated carbon from ponkan peels	Pb	60 min.	112.1 mg/g	(Pavan *et al.,* 2008)
23	Grapefruit peel powder	Uranium	80 min.	140.79 mg/g	(Zou *et al.,* 2012)
24	Mango peel powder	Cu, Ni, Zn	60 min.	46.09 mg/g; 39.75 mg/g; 28.21 mg/g	(Iqbal *et al.,* 2009)
25	Lentil shell powder	Cu	180 min.	9.59 mg/g	(Aydın *et al.,* 2008)
26	Activated cucumis sativa peel powder	Cd	60 min.	58.14 mg/g	(Pandey *et al.,* 2014)
26	Wheat stem powder	Cu	60 min.	0.1032 mmol/g	(Tan *et al.,* 2009)
28	Olive stone powder	Cu, Pb, Ni, Cd	60 min.	3.19×10^{-5} mol/g; 4.47×10^{-5} mol/g; 3.63×10^{-5} mol/g; 6.88×10^{-5} mol/g	(Fiol *et al.,* 2006)
29	Rice straw powder	Cd	180 min.	13.84 mg/g	(Ding *et al.,* 2012)
30	Activated sunflower hull	Cu	180 min.	57.14 mg/g	(Witek-Krowiak, 2012)
31	Activated neem bark powder	Cu, Zn	48 hrs.	21.23 mg/g; 11.9 mg/g	(Maheshwari *et al.,* 2015)
32	Mosambi peel powder	Cr	120 min.	250 mg/g	(Saha *et al.,* 2013)
33	Garlic peel powder	Pb	120 min.	51.73 mg/g	(Liu *et al.,* 2014)
34	Muskmelon peel powder	Pb	120 min.	167.8 mg/g	(Huang and Zhu, 2013)
35	Sugarcane bagasse	Hg	60 min.	35.71 mg/g	(Khoramzadeh *et al.,* 2013)
36	Sulphered orange peel powder	Pb, Zn	-	164.0 mg/g; 80.0 mg/g	(Liang *et al.,* 2011)
37	White rice husk powder	Brilliant green dye	30 min.	66 mg/g	(Tavlieva e al. 2013)
38	Activated soy meal hull powder	Acid blue 92	24 hrs.	114.94 mg/g	(Arami *et al.,* 2006)
39	Activated carbon from groundnut-shell	Basic green 4	30 min.	222.2 mg/g	(Malik *et al.,* 2007)
40	Activated carbon from pinewood powder	Basic blue 9	120 hrs.	556 mg/g	(Tseng *et al.,* 2003)
41	Banana peel powder	Basic blue 9	24 hrs.	20.8 mg/g	(Annadurai *et al.,* 2002)

42	Bagasse pith powder	Acid blue 25	120 hrs.	673.6 mg/g	(Juang *et al.,* 2001)
43	Yellow passion fruit powder	Basic blue 9	48 hrs.	44.67 mg/g	(Pavan *et al.,* 2008)
44	Activated orange peel powder	Basic blue 9	24 hrs.	18.6 mg/g	(Annadurai *et al.,* 2002)
45	Carbonized coir pith powder	Rhodamine-B	120 min.	2.56 mg/g	(Namasivayam *et al.,* 2001)
46	Activated carbon from biomass euphorbia rigida	Disperse orange 25	-	118.93 mg/g	(Gercel *et al.,* 2008)
47	Activated carbon from hazelnut-shell powder	Basic blue 9	24 hrs.	8.82 mg/g	(Aygun *et al.,* 2003)
48	Activated carbon from walnut-shell	Basic blue 9	24 hrs.	3.53 mg/g	(Aygun *et al.,* 2003)

Furthermore, Table 1 represents applied agricultural waste based adsorbent material, pollutants removed, contact time along with their adsorption capacities with reference. The adsorption capacity of agricultural materials increases with the further modification via heat treatment and chemical treatment in their raw form. However, the information regarding the agricultural materials is not complete in all the available literatures, some examples are mentioned in table 1 for their comparative assessment.

Velazquez-Jimenez *et al.,* 2013, used raw and modified agave bagasse treated with HCl, HNO_3, NaOH, and applied it in the removal of Cd(II), Pb(II) and Zn(II) metal ions from water (pH=5). Characterization study emphasized that carboxyl groups, contained by bagasse material were the important factor for the highest removal of heavy metal ion. Raw bagasse showed adsorption capacity 14 for Cd (II), 36 for Pb (II) and 8 for Zn (II). After modification with HCl, HNO_3 and NaOH the value of adsorption capacity improves from 27 to 62%. The regeneration study had also been performed and highest regeneration was achieved for raw bagasse to nearly 45%.

Basu *et al.,* 2015, modified lentil husk with using different acidic chemicals treatment and used it in the removal of lead metal ion. Lentil husk showed a promising adsorbing material having modified hydroxyl and carboxyl functional groups, which are majorly responsible for the lead metal ion removal with higher efficiency. The adsorption capacity of lentil husk was found to be 81.43 mg/g with an initial lead metal ion concentration 250 mg/l at pH value 5 and 30^0 C temperature.

Other agricultural waste material rice husk was modified via chemical treatment and applied in precious uptake of gold metal ion from water (Xu *et al.,* 2015). The functional groups of modified form of rice husk showed excellent adsorption results with highest adsorption capacity 3.25 ± 0.07 mmol/g. Therefore, rice husk modified via the studied method is a promising low-cost adsorbing material for the water treatment as well as extraction of precious metal ions. Tasaso. 2014, studied about the role of pomelo peels in water treatment. Raw and modified form of pomelo peel was applied in the Cu (II) ion removal. The result showed highest removal efficiency with adsorption capacity of raw and modified pomelo peel powder was 19.7 mg/g and 21.1 mg/g respectively at pH value 4, 25^0 C temperature and 125 mg/l initial concentration of Cu (II) metal ion for the 60 min. of contact time in water treatment application. Therefore, the use of low-cost agricultural waste materials are quite interesting and promising in the removal of various harmful pollutants and uptake of various precious metal ions from aqueous solution of water. Njoku *et al.,* 2014, used chemically treated activated carbon from sky fruit husk powder and applied in the removal of bentazon from aqueous solution of water with the maximum outcome of adsorption capacity 166.67 mg/g. Yadav *et al.,* 2015, studied the phosphate removal from aqueous solution of water using the activated carbon obtained from fruit juice residue and rice husk. Adsorption process was analyzed on various parameters such as Contact time, adsorbent and pollutant dose, pH, temperature. The maximum removal efficiency was achieved with fruit juice residue as 95.85% with adsorbent concentration 3 g/l at pH value 6 and temperature 24.85^0 C. Hence, with the maximum removal outcome the fruit juice residue material is potential material for heavy metal removal in water treatment studies. Kizito *et al.,* 2015, studied the adsorption ability of wood and rice husk biochars in the removal of ammonium. The adsorption capacities were 44.64 ± 0.602 mg/g and 39.8 ± 0.54 mg/g for wood and rice husk powder biochars respectively. On the basis of their adsorption capacities value both biochars are a promising material for waste water treatment.

Finally with tis literature survey we have analyzed that as seen in table 1, the natural raw materials can be utilized with further modification in the functional groups present via chemical treatment or heat treatment. Hence, we can improve the desirable physicochemical properties of the agricultural waste based activated carbon materials such as their pore-size, functional groups, specific surface area etc. with the modification in raw natural material its physical, chemical as well as biological characteristics will change. Mostly chemical modification are more popular and used in the preparation of activated carbon material (Gautam *et al.,* 2014). In this various organic and inorganic acids such as hydrochloric acid, sulphuric acid etc., basic materials such as sodium hydroxide, calcium chloride, sodium carbonate, many others and oxidizing reagents such as hydrogen per oxide and many more minerals and various compounds have been used to modify the functional group and improve adsorption capacity of raw material.

4. Outlooks and discussion

The activated carbon based materials are the most popular and efficient adsorbent materials, widely used in wastewater treatment applications due to its tremendous properties such as wide specific surface area, ability to link with various compound materials, easy to prepare, stability and reusability (Grassi *et al.,* 2012). Hence, to overcome the cost issues of activated carbon materials low-cost agricultural materials are the most suitable and sustainable alternative due to its nature based availability. Although, various literatures have been reported but our aim is to focus on to maximize the emphasis on the use of nature based available organic waste materials obtained from agriculture to replace the high cost commercial activated carbon. Agricultural waste materials are most convincing option due to their ability to remove efficiently many and different contaminants with high rate of adsorption (Grassi *et al.,* 2012). Thus, taking into account a revised literature on agricultural waste materials have been shown in Section 3 and table1. Hence, from our literature study we will be able to answer some important questions such as, does the absorbent has the ability to link with numerous compounds? If so, then does this linking ability of adsorbent belong to same group of pollutants or others too?

It is quite interesting to analyze that in what manner the agricultural waste materials such as rice husks, orange peels, garlic peels, banana peels and many others are being used as adsorbents for the removal of different dye materials such as acid dyes, basic dyes and many others and heavy metal ions too. Therefore, it is quite interesting to analyze the affinity of agricultural wastes for dyes and heavy metal ions removal from water with their high adsorption capacity mentioned in table 1. With the numerous literature study, we have analyzed that very few studies are based on the specific area based wastewater treatment whereas, there are huge literature available focused on the water treatment from aqueous solution of single compound pollutant. There are numerous literatures available on the use of commercial high cost activated carbons as compared to the use of low-cost activated carbons obtained from agricultural waste materials. This real case studies are highlighted in recent literatures (Gupta *et al.,* 2006, Kyzas and Kostoglou, 2015). Even though, the performance of commercial activated carbons are much better than agricultural waste materials based activated carbons (Gupta *et al.,* 2006) in the form of comparison with their adsorption capacities, but the promotion of utility of activated carbons from low-cost agricultural waste materials have the potential to solve the air pollution issue as well as tackle the forest fire and many more issues related to the environment. By another case study we obtained the results that the performance of activated carbons obtained from agricultural wastes are similar to the commercially available activated carbons (Arris *et al.,* 2014). In spite of above, there are few concerns too for the sustainability of adsorbent materials such as (i) their regeneration, (ii) their life span for reusability as compared to the commercially available activated carbon. First point highlights the concern of regeneration cost of adsorbent materials. Noticing the issue, Tolba *et al.,* 2015, prepared nano-silica from rice husk and analyzed its adsorption capacity in the methylene blue, a basic dye removal. The results were 99.6% removal of methylene blue dye in 40 min of time. Nano-silica has showed its potential utility in water treatment as it recycled easily with normal heat treatment and highly efficient in its four successive batch of water treatment. The adsorbents cost is important indicator because it depends on various factors such as, its availability i.e. nature based or non-natural, synthesis, regenerate and reuse, production place. Çifçi and Meriç 2015, highlighted that the cost of pumice is nearly 100 times lower than other commercial activated carbons.

5. Conclusion

This literature review study observes some concluding remarks such as:

- There is much less data available about the characteristics of the novel agricultural waste material base activated carbons. Many adsorbents test was performed without highlighting the important information about the average particle size and specific surface area of adsorbent material, dose of adsorbent material, contact time of adsorption process, pollutant dose etc. Therefore, still much extensive study is required to get all the information.
- There is less information available about adsorbents and pollutants affinity. Therefore, the adsorbents and pollutants matrices could be helpful in the identification of specific adsorbent material for a particular pollutant on the basis of their affinity to that pollutant, for the higher output removal efficiency in water treatment. For example some low-cost activated carbons obtained from agricultural waste materials such as orange peels, rice husks and banana peels showed higher affinity in case of various pollutants dye, heavy metal ions and other organic- inorganic pollutants as compared to the commercially available high cost activated carbons
- This is an era of focusing on green technology. This promising role can be better played by novel agricultural materials based activated carbons acts as adsorbents in wastewater treatment at their full efficiency. Most of the studies in the field of wastewater treatment are based on experiments at lab level, whereas only few studies particularly focused on the real area based pollutant detection and their treatment.
- Therefore for further studies we need to focus on the regeneration of this novel low-cost agricultural based adsorbing materials and also careful testing should be done on their limit of reusability in water treatment applications.

Acknowledgements

The authors are very thankful for the financial support from Dean Student welfare, University of Lucknow, Lucknow under a Shodh-Medha scholarship scheme to carry out this research work.

Conflict of interest

The authors declare that they have no conflict of interest.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable

Credit authorship contribution statement

Ms. Sharda Pandey: Idea of article, Literature search, analysis and interpretation of results, Conceptualization, Methodology, Investigation, Formal analysis & Writing-Original Draft. (First Author) (Corresponding Author)

Prof. Rajesh Kumar Shukla: Supervision in Study, Review &Editing. (Co-author)

Prof. Anchal Srivastava: Supervision in Study, Review &Editing. (Co-author)

Funding

Funding information is not applicable.

Availability of data and materials

This is a literature review based study. Data is mentioned in the form of references.

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