Synthesis, Characterization and Application of Low Cost Adsorbents Derived from Rice Husk and Groundnut Shell: a Review

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Abstract:

Use of various adsorbents for low cost and efficient removal of various pollutants from wastewater is very important research area. Various heavy metals, organic compounds, dyes can be removed from wastewater by using low cost materials. The studies carried out by various researchers reveals that chemical and thermal activation increases adsorption capacities of these materials. The removal percentages obtained in various researches ranges from 80 percent to 100 percents. The investigation on characterization of adsorbent is also reported. Groundnut shells and rice husk are two low cost agricultural materials. The adsorbent derived from these starting materials are found to be very efficient for removal of phenols and heavy metals such as cadmium, chromium, lead, copper, arsenic etc. The current review aims at summarizing the research and studies on preparation, characterization and application of sorbents obtained from these two low cost agricultural materials.

Keywords:

Activation, properties, surface area, percentage removal, economy, efficiency.
Introduction

Wastewater treatment methods for removal of various pollutants include various techniques such as electro dialysis, coagulation, ion exchange, flocculation, membrane separation techniques, adsorption and biological treatments [1,2,3,4]. Adsorption is very effective method for removal of organic matter from the effluent[5,6,7,8]. Various low cost adsorbent were also found very efficient for removal phenols from the wastewater[9,10,11,12]. Very effective removal of phenol has been reported by using tamarind shell adsorbent, flyash adsorbent, coconut shell adsorbents [13,14,15,16]. Also various heavy metals were removal successfully by using low cost materials[17,18,19,20].

Groundnut shells and rice husk are two waste byproducts of agriculture industry. Also disposal of this waste is a nuisance. These materials can be used as an adsorbent with or without modification with different degree of removal efficiencies for removal of pollutants like dyes, organic matter, heavy metals, phenols etc.[21,22,23,24,25].The current review aims at summarizing research and studies carried out to prepare, characterize and use these materials for effective removal of various pollutants from wastewater.

Preparation, Characterization and Application of Adsorbents

Rice Husk Adsorbents

Sivakumar et.al. carried out investigation on treatment of tannery waste by using rice husk adsorbent for chromium removal[26]. According to these studies, optimum parameters for adsorption were, an optimum adsorbent dosage of 15 g, contact time of 150 min., agitation speed of 750 rpm and dilution ratio of 5. Their study revealed that the percentage removals of concentration of Cr (VI) by rice husk silica powder with the adsorption dosage of 5, 10, 15 and 20 g were found to be 47.4, 56.3 and 64.5 and 60.8% respectively. It was also observed that the optimum contact time for which, maximum removal of Cr (VI) in tannery industry wastewater occurs is 150 min. Also, maximum removal of Cr (VI) in tannery industry wastewater was observed at 750 rpm agitation speed. According to studies carried out by Kulkarni and Kaware to analyze fixed bed adsorption of cadmium on rice husk adsorbent, with increase in initial concentration from 10 mg/l to 50 mg/l, the exhaustion time decreased from 830 mg/l to 570 mg/l and break point time decreased from 330 minutes to 120 minutes[27]. They also observed that with increase in flow rate, exhaust time and break through time decreased significantly. Also, they observed increasing shift from second to first order with increase in initial concentration. They found the optimum bed height, initial concentration, flow rate and pH values to be 50 cm,30 mg/l, 60 ml/min and 6 respectively.

Modified rice husk as adsorbents was used for phenol removal by Yousaf and Ibrahim[28].They used raw husk (RH), Grafted (G) and Charred (C) rice husk. According to their studies, modified rice husks could be used as potential adsorbents for phenol removal from aqueous system. Ye et.al. used modified rice husk for copper removal from aqueous solution [29]. They
examined the adsorption isotherms, thermodynamic parameters, kinetics, pH effect, and desorbability. The adsorption data followed both Langmuir equation and Freundlich equation. The study showed that the desorbability of Cu(II) was about 15-20%. Mehdinia et.al. carried out research on removal of hexavalent chromium pollution from aquatic solutions by rice husk silica adsorbent [30]. They investigated effectiveness of new adsorbent prepared from rice husk silica, raw rice husk and rice bran to remove chromium from aquatic solutions. They prepared rice husk silica by burning of clean rice husk inside a muffle furnace at 800°C. Also acid leaching was done to leach off the different materials. They obtained the chromium removal of 98 percent by using these adsorbents.

Kadhim and Al-Seroury carried out investigation on use of rice husk in fluidized bed for removal of phenol from the wastewater[31]. The data obtained fitted well to both the Langmuir and Freundlich isotherm models. It indicated favorable and monolayer adsorption. They carried out a series of experimental run to evaluate the biosorption of rice husk (RH) and activated rice husk (ARH). This study showed that the pretreatment of rice husk has increase specific surface of the developed adsorbents. Shafiei and Ghadaksaz used rice husk for cadmium removal at different conditions[32].According to them, further studies should be conducted to determine the contribution of each of the parameters examined in the present study to the process using untreated and chemically treated rice husk. Anand et.al. carried out investigation on rice husk ash as carbon adsorbent for removal of hexavalent chromium from simulated waste water[33]. For initial concentration of 10 mg/L, they observed that 6 mg/L was optimum adsorbent dose. The optimum pH was 6 and contact time was 80 minutes. Removal of Congo-Red dye was investigated by Sharma and Beena using activated rice husk carbon as a low cost sorbent[34]. The investigation was carried out under variable system parameters such as agitation time and dose of adsorbent. First order kinetics was followed by removal process. They obtained about 99 percentage removal in 200 minutes contact time.

Rahman et.al. treated textile wastewater with activated carbon produced from rice husk [35]. They observed the optimum temperature and contact time for adsorption to be 40°C and 60 minutes respectively. Yadav et.al. carried out research on removal of aniline blue from aqueous solution onto rice husk carbon[36]. The XRD spectra for the adsorbent indicated amorphous disordered structure. According to these studies, percent adsorption increased with increase in temperature. It also increased with increase in the contact period. The study also suggested that aniline Blue dye adsorption on the rice husk carbon was endothermic. Dezhampanah et.al. used sugarcane bagasse and modified rice husk for the removal of malachite green from aqueous wastes[37]. It was observed by them that removal of malachite green increased with decreasing initial dye concentration, increasing adsorbent dosages and contact time up to equilibrium. Optimum pH for removing dye was 7. Rice husk adsorption of dye followed Langmuir isotherm. Sethi
and Sharma carried out studies on steam activated pigmented rice husk carbon for dye removal[38]. Amaranth dye from aqueous solution was adsorbed on adsorbent. They observed that the nature of the adsorbent and its concentration affected the time needed to reach equilibrium. The pseudo first order equation was able to describe the adsorption isotherm.

Food industrial wastewater was treated by Asrari et al. for removal of zinc and lead[39]. They studied the influence of pH, contact time and adsorbent amount on the removal. The optimum pH values for these two adsorbates were 7.0 and 9.0. Also it was observed that optimum agitating time for adsorption of Pb\(^{2+}\) and Zn\(^{2+}\) ion was 60 min. As expected the metal ion concentration in solution decreased with increase in the sorbent amount for a given initial metal concentration. Zinc and lead removal reached maximum to 70% and 96.8%, respectively during the experiments. Taha et al. investigated dye removal from industrial wastewater using rice–husk as low cost adsorbent[40]. They observed that the percentage of dye removal increased from 68% to 100 % as the adsorbent dosage increased from 0.5 to 2 g for 100 ml of effluent. The dye adsorption was rapid for first 20 minutes and then became slow. Also they observed higher adsorption capacity for size smaller than 1000 μm. M. Abbas and F. Abbas carried out investigation on application of rice husk to remove humic acid from aqueous solutions[41]. They obtained removal efficiency of 98.24%. They observed that the efficiency decreased with increasing of initial concentration flow rate and pH. Also with bed height and feeding temperature, the adsorption efficiency increased.

Otaru et al. investigated development and characterization of adsorbent from rice husk ash in order to bleach vegetable oils[42]. They observed that at constant carbonization time of 1 hour, as carbonization increased from 500 to 700 ℃, the ash content of the rice husk decreased from 6.78 to 5.72. Also at constant carbonization time of 2 hour, as carbonization increased in temperature from 500 to 600 ℃, the ash content of the rice husk increases from 5.451 to 5.740 and lastly for carbonization time of 3 hour, as carbonization increased in temperature from 500 to 600 ℃, the ash content of the rice husk increases from 5.420 to 5.999. Based on the ash content, carbon content and porosity, the optimum time was 3 hours. It was also observed that acid pretreatment increased the adsorption ability of adsorbent. S. Singh and A. Singh carried out investigation on rice husk carbon as an adsorbent for chromium removal[43]. They activated rice husk ash by using H\(_3\)PO\(_4\) (40%). At low values of pH (around 2) for the carbon dosage of 1000mg/L, the maximum adsorption of chromium (VI) was obtained (93-94%). Kumar et al presented review on properties and industrial applications of rice husk[44]. According to this review, rice husk has become value added material with increasing domestic and industrial applications of rice husk and rice husk ash. Jha used rice husk(RH) adsorbent for phenol removal[45]. He used four step process for adsorbent preperation, 1. pyrolysis of rice-husk 2. steam gasification of rice-husk 3. leaching of char with HCL 4. digestion of char with NAOH. The fixed carbon was 37
percent in the prepared adsorbent. Activated RH char contained about 83 percent carbon. He concluded that the pyrolysed rice-husk sorption capacity for phenol can be brought near to that of commercial grade carbon properties by activating it thermally and chemically. Janveja et.al. carried out studies on congo red dye removal for textile industrial waste. They used activated rice husk charcoal as an adsorbent[46]. The adsorption increased up to increase in adsorbent dose from 0.2 to 1.2 g/l and then became constant. Similarly it increased up to contact time of 210 minutes and then became constant.

Jha carried out investigation aimed at studying potential of rice-husk as an adsorbent for phenol removal from aqueous solutions[47]. According him, rice-husk adsorption capacity for phenol can be improved to a great extent by activating it thermally and chemically. Galletti investigated zinc removal from effluent by rice husk as adsorbent[48]. According to these studies, the rice husk was an effective and economical adsorbent for the removal of Zn metal ions from aqueous solution. They obtained maximum adsorption at pH equal to 8. M. Abbas and F. Abbas carried out investigation on utilization of Iraqi Rice husk (irh) in the removal of heavy metals from wastewater[49]. They studied removal of Al, As, Cd, Cr, Cu, Fe, Ni, Pb and Zn ions from industrial wastewater. For these metals they obtained maximum removal of 96.24, 95.78, 96.21, 98.73, 95.75, 97.61, 95.82, 95.05 and 96.33% respectively. Percentage removal increased with increase in the flow rate.

**Groundnut Shell Adsorbents**

Qaiser et.al. investigated biosorption of lead(II) and chromium(VI) on groundnut hull[50]. They carried out equilibrium, thermodynamic and kinetic studies. They used nitric acid for soaking and then washed the adsorbent with distilled water. The surface area was found to be 3.85 m²/g by BET method and 24.75 m²/g by Langmuir method. These studies revealed that this adsorbent has higher adsorption capacity than many other adsorbents like bagasse fly ash, coconut shell charcoal, coconut husk fibers, sugar beat pulp, maize cob, sugar cane bagasse, for both lead(II) and chromium(VI).

Itodo used biosorbent prepared from chemically treated groundnut shells for decolourizing water[51]. They treated an industrial dyeing waste water obtained from the effluent discharge reservoir of Chellco textile company Kaduna, Nigeria. They used chemical activation method for the adsorbent. According to their conclusion, the results obtained were in close agreement with available data from the literature. They concluded that the precursor, groundnut shell was good for biosorbent production with a high sorption ability, especially when catalyzed with salt (ZnCl₂). A polycyclic aromatic hydrocarbon(anthracene) was treated by Owabor and Aluyor using 1:1 mixture of the contaminant anthracene and activated carbon from groundnut shell in a water medium[52]. They found that the presence of activated carbon with microorganisms increased the rate of disappearance of the hydrocarbon. Idris et.al. carried out an investigation for removal of chromium and nickel from dye effluent by using groundnut.
shell adsorbent[53]. They used two step process for activation. First they used thermal activation at high temperature followed by chemical activation using sulphuric acid. Percentage yield of activated carbon was 62 to 65 percent. The bulk density was approximately 10 g/cc. While preparing the adsorbent they kept the adsorbent in H₂SO₄ as an activating agent for different activation time(5,10,15 minutes). They observed that Chromium adsorption increased with increase in contact time of the adsorbent. The adsorption was pseudo- first order. Kulkarni and Kaware used groundnut shell activated carbon for removal of phenol from synthetic effluent in a fixed bed[54]. According to these studies, parameters like initial phenol concentration, bed height and flow rate have significant effect on the kinetics of phenol removal. They carried out experiments by varying these parameters. They observed that The increase in bed height delays the time for adsorption. Also increase in initial concentration reduces the time required for adsorption up to certain initial concentration. Haldhar et.al. carried out investigation on adsorption of arsenic, As (III) from aqueous solution by groundnut shell[55]. They used washed groundnut shells without any treatment for arsenic removal. This untreated groundnut showed 30 percent arsenic removal. For increase in adsorbent dose from 0.5 gm to 1.5 gm (per 50 ml of the solution), there was steep increase in adsorption. The rise became marginal after that. Also they observed that 20°C was the optimum temperature for adsorption. Also the As (III) removal efficiency decreased with the increase in initial concentration. The Langmuir isotherm fitted the data better, indicating a reversible phenomenon and the monolayer coverage. Sundaram and Sivakumar used indian almond shell waste(IASW) and groundnut shell waste(GSC) for the removal of azure a dye from aqueous solution(AA)[56]. According to this investigation, the percentage removal of dye AA on IASC and GSC decreased with the increase in the initial concentration.

Ajmal et.al. carried out investigation on the use of Testa of groundnut shell (arachis hypogoea) for the adsorption of nickel ni(ii) from the aqueous system[57]. They observed that, with initial concentration, the adsorption capacity of Ni (II) increased from 0.68 mg/g to 9.7 mg/g. Also there was increase in the % adsorption from 68% to 97%. Also pH value of 6 was observed to be optimum. As expected, the percentage adsorption increased with adsorbent dose. Kiran et.al. studied utilization of groundnut shell as biosorbent for heavy metals Removal[58]. They carried out experiment to study lead and copper removal from the synthetic effluent. They observed that the removal efficiencies for these two heavy metals were 68.2% and 77.8% with the optimum dosage of 50 g and 30 g respectively for 100 ml of sample. The batch experiment data followed Freundlich isotherm rather than Langmuir isotherm. They also found that the Cu adsorption fitted in Lagergren first order model and pseudo second order kinetic model was followed by lead removal. Uwadiae et.al. carried out comparative studied on sorption of heavy metal ions by granular activated carbon from coconut shell, sawdust and groundnut shell[59]. According to these studies, groundnut shells were effective for the removal of manganese ion, zinc ion and
lead ion. They were most effective for removal of cadmium.

**Conclusion**

Use of agricultural waste for removal of various pollutants from wastewater serves two purposes. Firstly, It reduces the problem of disposing the agricultural waste to some extent. Second advantage of use of these materials for adsorbent preparation is reduction in treatment cost. The research carried out on preparation, characterization and application of adsorbents prepared from these two adsorbent has yielded promising results. More efficient methods for regeneration, recovery and disposal for used adsorbent can make these adsorbents more economical and acceptable alternative over conventional adsorbents.

**References**


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