

Low Cost Adsorbents Utilization for the Treatment of Pharmaceutical Wastewater

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Abstract

Low cost adsorbents from agricultural waste like rice husk was developed with various activation methods and tested for the removal of aqueous contaminants. Adsorption of organics using rice husk has been investigated. Various experiments were studied using batch adsorption technique under different conditions of reaction time, pH, adsorbent dosage, initial pollutant concentration, and temperature. This process will provide the low cost adsorbent for the treatment of the optimum conditions found is reaction time of 45min, pH of 7, and adsorbent dosage of 1000mg/l.

Keywords: adsorbent, low cost, pharmaceuticals, wastewater.

INTRODUCTION

Water is the most essential element to life on earth. In its purest form it is odourless, colourless and tasteless. Level of contaminants in aquatic ecosystems has increased due to discharge of industrial effluents in water which in turn has led to water demand for domestic and industrial purpose (1, 15). It is recognized that public perception of water quality is greatly influenced by the organic content. The presence of very small amounts of organics in water (less than 1ppm) is highly toxic and undesirable (8, 14).

Pharmaceutical compounds are typically produced in batch processes leading to the presence of a wide variety of products in wastewaters which are generated in different operations, wherein copious quantities of water are used for washing of solid cake, or extraction, or washing of equipment. The presence of pharmaceutical compounds in drinking water comes from two different sources: production processes of the pharmaceutical industry and common use of pharmaceutical compounds resulting in

their presence in urban and farm wastewaters. The wastewaters generated in different processes in the manufacture of pharmaceuticals and drugs contain a wide variety of compounds. Further, reuse of water after removal of contaminants, whether pharmaceuticals or otherwise, is required by industry. In view of the scarcity of water resources, it is necessary to understand and develop methodologies for treatment of pharmaceutical wastewater as part of water management. This has to be removed from the wastewater before its discharge in to the environment (9, 16).

The adsorption process is one of the effective methods for removal organics and color from the waste effluent. The process of adsorption has an edge over the other methods due to its sludge free clean operation and completely removed pollutants, even from the diluted solution. Activated carbon (powdered or granular) is the most widely used adsorbents because it has excellent adsorption efficiency for the organic compound. Nevertheless, commercially available activated carbon is very expensive. Furthermore, regeneration using solution produced small additional effluent while regeneration by refractory technique results in a 1015% loss of adsorbents and its uptake capacity. Numerous researchers worked earlier on variety of adsorbents as mentioned below. Wool Fiber and Cotton Fiber (3), Banana pith, Biogas residual slurry (4), Hardwood (5), Neem (*Azadirachta Indica*) husk (6), Tamarind Fruit Shell (7).

The presence of silica in rice husk (RH) has been known since 1938.¹ Rice husks produce a high ash content, varying from 13 to 29 wt.% depending on the variety, climate, and geographic location. The ash is largely composed of silica (87±97%) with small amounts of inorganic salts.² Due to its high silica content RH has become a source for preparation of a number of silicon compounds such as silicon carbide, silicon nitride, sialon, zeolite (2).

In this study the treatment of pharmaceutical wastewater using activated carbon and rice husk ash.

MATERIALS AND METHODS

Pharmaceutical sample has been collected from the jeedimetla industrial estate. The initial characterization of the effluent has been done using standard methods for water and wastewater 2005 (APHA,2005).

Collection and Preparation of Adsorbents Rice husk and rice husk ash were collected from rice mill situated in Miryalaguda locality, Nalgonda district of Telangana state. The rice husk was screened and washed with water to remove the dirt and was sun dried for a day. The rice husk ash (RHA) was directly used for adsorption study. Only fine ash was used as adsorbent. Characterization of the RH carried using X-ray diffraction spectroscopy, HITACHI S 3400N scanning electron microscope. The composition of sample information is produced from signals of electrons that interacted with the atoms present in the sample.

The four factors effect of contact time, concentration, pH and adsorbent dose have carried. The experiment performed by changing one of the parameters at a time while

the other parameters were fixed. The batch adsorption tests have been carried out by shaking 100ml working solution in a stoppered conical flask. The conical flasks were placed on rotary shaking machine for one hour at 150 rpm. The progress of adsorption during the experiment was determined by removing the flask after desired contact time and analyzing the supernatant solution spectro-photometrically and APHA, 2005. Different concentration of the pollutants maintained using dilution method. Adsorption tests were performed at temperature 29°C ±2. The spectrophotometric readings were recorded and further calculations were done to see the removal efficiency of the adsorbents. The removal efficiency was calculated using following formulae:

$$\% \text{ Removal efficiency} = \frac{(C_i - C_f)}{C_i} \times 100$$

Where, C_i is the initial concentration of pollutant in solution and C_f is final concentration of pollutant in solution.

RESULTS AND DISCUSSION

Table. 1: Initial characterization of the pharmaceutical sample

S. No.	Parameters	Concentration (mg/l)
1	pH	7.2 ± 0.2
2	COD	1700 ± 10
3	TOC	1200 ± 10
4	BOD	940 ± 5
5	TS	1940 ± 10

Instrumental analysis of the Rice husk ash:



Fig.1 RH samples before making fine powder

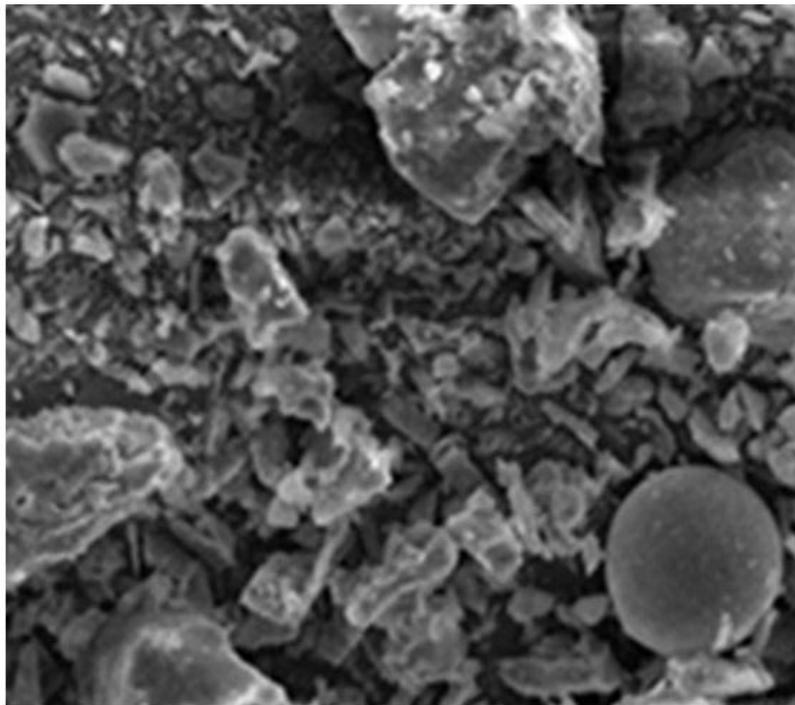


Fig.2 Scanning electron microscope view of the RH

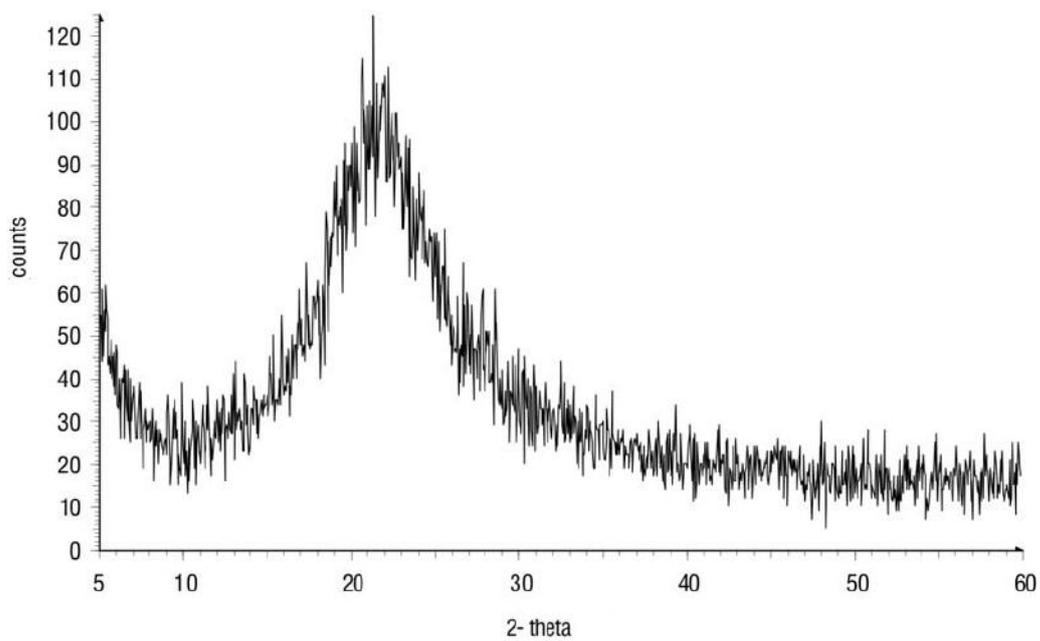


Fig.3 XRD picture of the RH sample

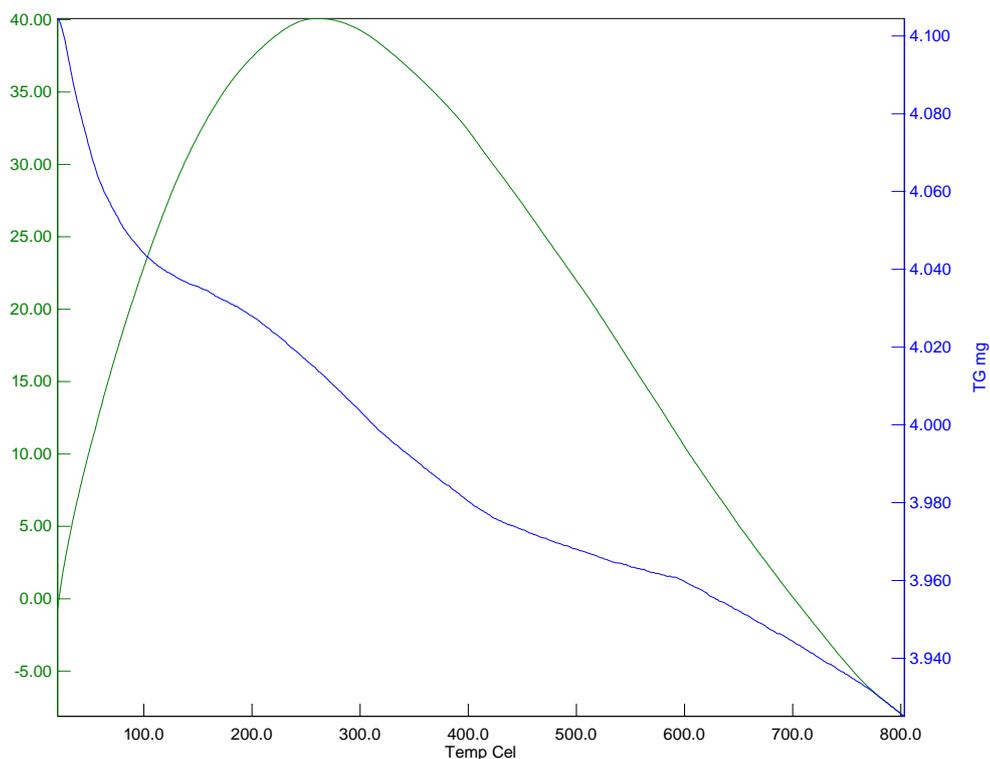


Fig.4 TG-DTA analysis of the RH sample

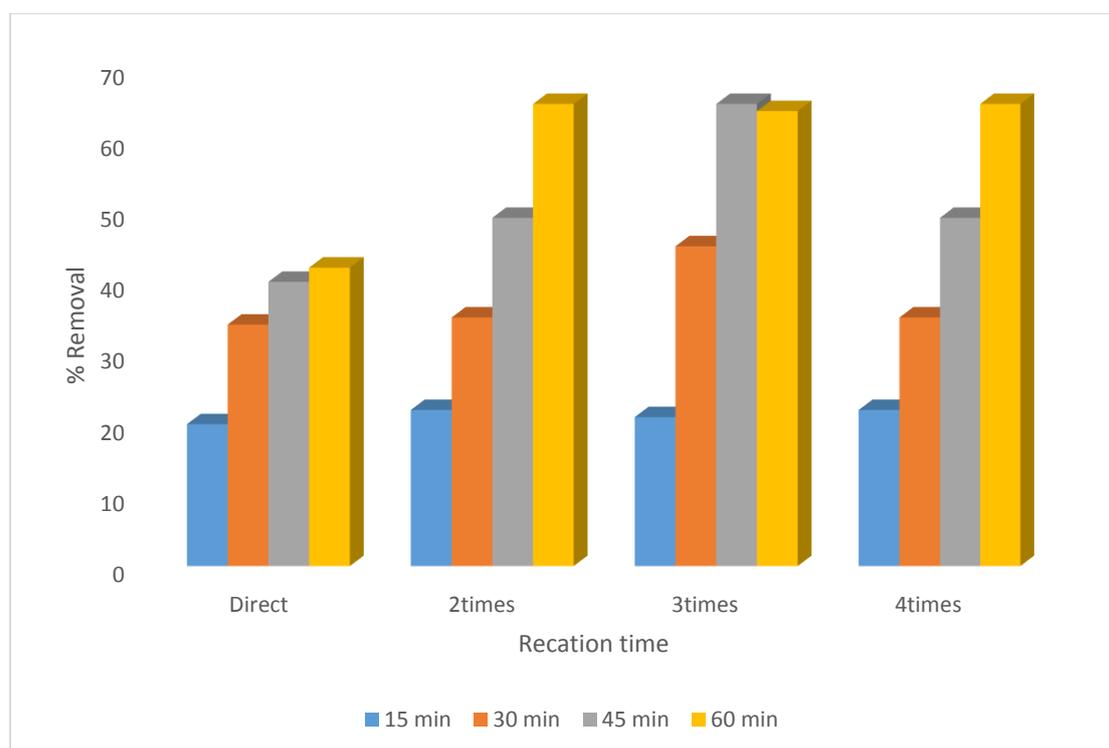
The Fig. shows the initial view of the RH and Fig. shows the SEM image of the RH. It was observed that some of the particle with smooth surface, which will be helpful for the adsorption process.

The X-ray diffraction patterns for rice husks are shown in Figure. A broad peak from 15 to 35 2theta diffraction angles indicates the presence of amorphous silica. In fact, the result obtained confirms those already reported in the literature for rice husk ash (17). The horizontal axis represents the sample temperature and the vertical axis shows (Fig.) the TG (weight change) and DTA (thermal behavior). The bottom of the TG curve indicates a weight decrease and the top indicates weight increase. For the DTA curve, the downward direction indicates an endothermic reaction and the upward direction indicates an exothermic reaction. It was observed that the TG decreased gradually and at 800°C it shown approximately 40%. The silica of the RH

Effect of Initial Concentration and Contact Time

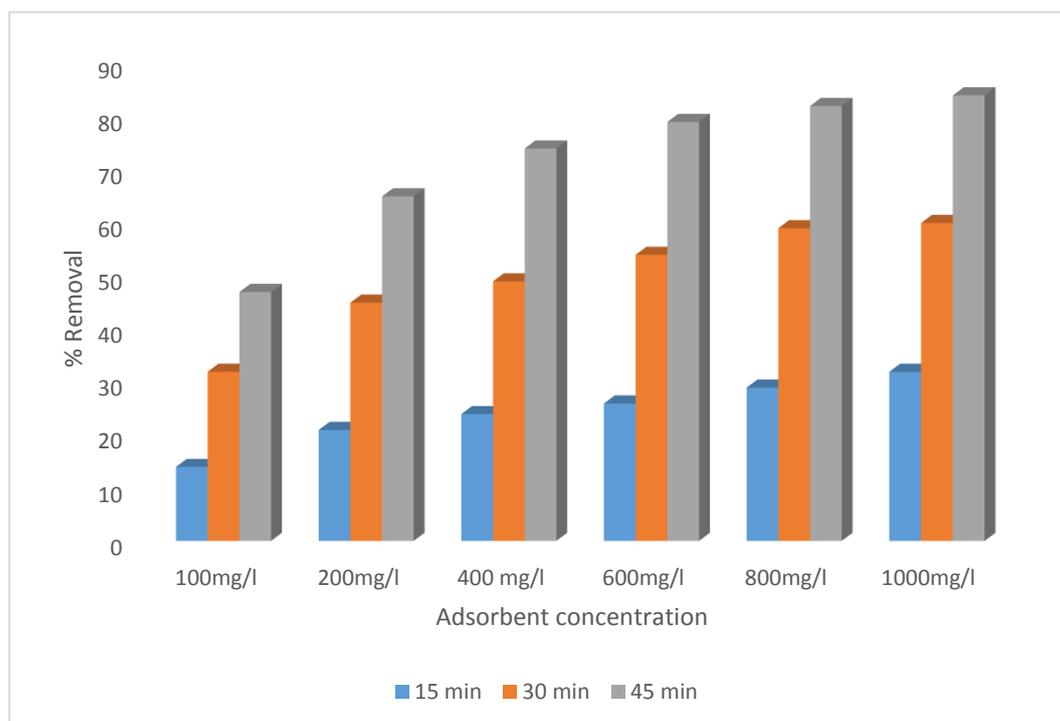
It is well-known that the pollutants concentration plays as an important role in the adsorption process, which can impel strongly the solute molecules to overcome mass transfer resistance between the liquid and the solid phases (10). Figures- show the effect of different initial concentrations on the adsorption capacity of RH. As seen from the Figure the percentage of adsorption decreases with increasing initial concentrations of pollutants with RH. Almost 65% of COD removal was observed for 4times dilution

with RH. Figure shows that the initial concentration has a marked effect on the contact time necessary to reach adsorption equilibrium. It can be found that a rapid uptake occurred for the initial concentration at 3times dilution, where over 65% of COD removed with RH within 45 min. Whereas, for the initial concentration of 2 and 4 times dilution, a relatively slow uptake can be observed and took 60 min to reach 64% removal with RH. At low concentration, the ratio of dye molecules to the number of available adsorption sites on adsorbent may be limited and consequently the adsorption process may mainly occur on the exterior surface. The rate of adsorption is fast in this stage, resulting in short time. With an increase in the amount of pollutant molecules, the situation changes and lots of dye molecules are probably adsorbed by the interior surface of adsorbent by pore diffusion after the adsorption of the exterior surface reaches saturation. Similar discussion has been reported by Hameed et al. for studying adsorption processes for methylene blue (11).



Effect of Adsorbent Dosage

To understand the effect of adsorbent dosage and initial concentration, the adsorbent dosage varied between 100mg/l and 1000mg/l and the typical results are shown in Figure. As expected, an increase in adsorbent dosage leads to an increase in the percentage removal of COD. Initially, a rapid enhancement of COD removal was observed with increasing the dosage from 100 to 1000 mg. As the adsorbent dosage increases, the adsorbent sites available for the dye molecules also increase and consequently better adsorption (10).



Effect of pH:

The pH of the solution plays as an important factor in the adsorption process, which may alter the surface properties of the adsorbent as well as the degree of ionization of the dye. The influence of pH on the organics adsorption onto RH was studied and amount of adsorbent 1000 mg/l in the pH range of 2–11 and the results are shown in Figures. Clearly, the amount adsorbed and the percentage removal efficiency of COD on adsorbent increased as the pH of aqueous solution increased from 2 to 11. This might be due to cationics presence in its structure. In carbon-aqueous systems the potential of the surface is determined by the activity of H⁺ ions, which react with the carbon surface. For the carbon surface the potential determining ions are H and OH₂ and complex ions formed by bonding with H1 and OH₂. The broken bonds along the surface of the carbon result in hydrolysis.

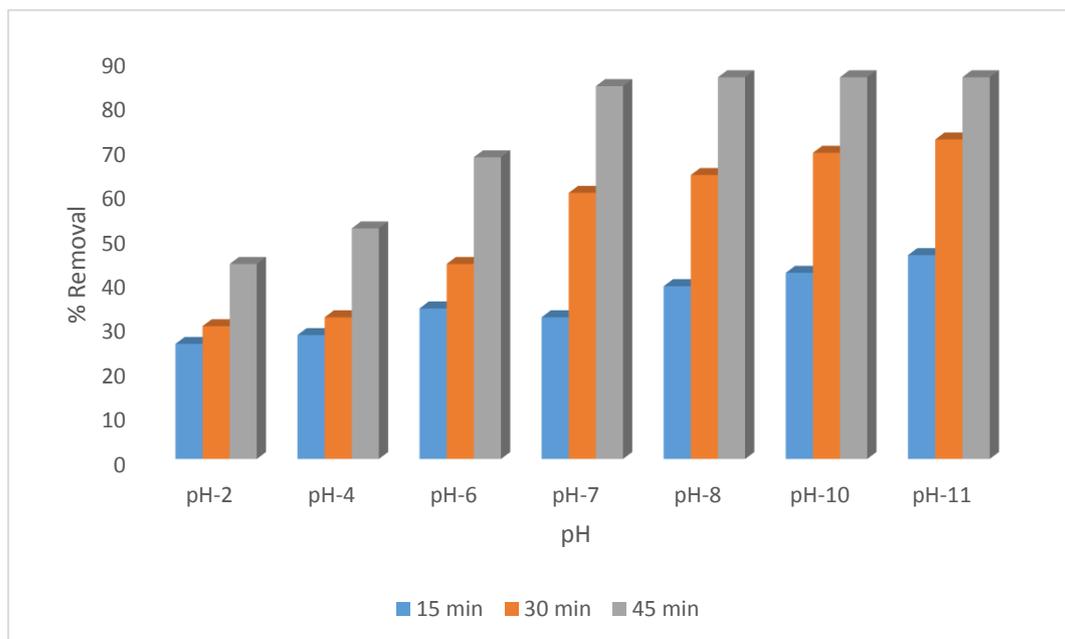
At low pH



At high pH



In our studies the rate of adsorption is high at higher pH. With the increase of pH value, the negative charge increases on the surface of adsorbent and the surface will then exhibit a cation exchange capacity (12, 13).



CONCLUSION

1. The optimum Reaction time, pH, and adsorbent dosage is 45min, 7 and 1000mg/l with three time diluted samples.
2. This study concludes that the rice husk ash is useful for the treatment of the pharmaceutical wastewater.

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