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Application and Comparison of Raw Rice Husk and Chemically Modified Rice Husk as an Adsorbent

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Abstract:

Natural water resources has been get polluted due to industrialization, which causes serious environmental and health issues. Many techniques are in practice since long to overcome this hazardous problem. Among all these method with the motto “Green Chemistry to blue protection” – Agro-waste materials like Rice Husk is explore to minimize the water pollution load as it is inexpensive and easily available material. The study finally lead us to the conclusion that the agro-waste rice husk is abundant in nature has high potential as an adsorbent for organic contamination removal. Further more the comparison of row powdered rice husk and chemically modified rice husk for their efficiency to remove chemical oxygen demand is the heart of this research. Both this low cost materials are powerful adsorbent follow Freundlich and Langmuir adsorption isotherms. Rice Husk Powder removes COD upto 59.077 % and chemically modified rice husk removes 73.743% COD Contributing components.

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Key words: COD, Rice Husk, chemically modified rice husk, Adsorption isotherm, Adsorption intensity ($1/n$), Adsorption energy ($b \times 10^3$), Adsorption capacity (K, Θ)

Introduction:

The pollution of water resources due to the disposal of organic content and heavy metals has been an increasing worldwide concern for the last few decades. The characteristics of industrial waste - water may differ considerably both within and among industries. The impact of industrial discharges would depend not only upon collective characteristics such as COD, BOD and suspended soil, but also on their content of specific inorganic and organic substances (1,2). Rice husk is recognized as an effective adsorbent for a wide range of solutes particularly water pollutants, they actually suffer from at least two major drawbacks, which are low exchange or sorption capacity as well as poor physical stability (i.e. partial solubility) (3). This is due to the inert nature of polymer inside cellulose structure of rice husk. The polymer is relatively inert as the three hydroxyl groups of each cellulose unit responsible for most of the interactions with organic and inorganic substances are involved in extensive inter- and intramolecular hydrogen bonding (4). In addition, both lignin and silica constitutes a major obstacle in using rice husk as an adsorbent material. This is mainly because lignin acts as a cementing matrix between cellulose fibrils and hemicelluloses molecules, while silica is present on the outer surface of rice husks in the form of silicon – cellulose membrane (5). Lignin and silica can reduce the binding between accessible functional groups on rice husks' surfaces and adsorbate ions / molecules. Over and above, the inner surface of rice husk is smooth and contains wax and natural fats that provide good shelter for the grain but the presence of these impurities also affects the adsorption properties of rice husk chemically and physically (6). Therefore, in order to overcome the associated problems, it is necessary for rice husk to be modified by several treatments to remove structural and compositional impediments to analysis and subsequent degradation processes in order to enhance digestibility, improve the rate of enzyme analysis, and increase yields of intended products (7). Moreover, Wan Ngah and Hanafiah (8) reported that, the treatments of rice husk can increase the cellulose content of the solid fraction by virtue of lignin removal and hemicelluloses solubilization. On top of that, rice husk modification can also reduce cellulose crystallinity as well as increase adsorbent porosity nature. Thus, due to the advantages of rice husk modification in terms of adsorption efficiency, many researchers began to explore this particular area of study. For example, Hsu and Pan in (9) found that, the adsorption capacity of methacrylic acid - modified rice husk was 14 times higher than that of the unmodified rice husk and more than three times higher than those of traditional adsorption of paraquat, by Fuller's earth, activated carbon, cationic exchange resin and bentonites. Chemical treatments of rice husk are able to reduce the content of hemicelluloses, lignin and cellulose crystallinity. The reduction in crystallinity leads to an increase the specific surface area for treated rice husk compared to raw rice husk (10). Daffalla et al., (10) reported that, the porosity of sulphuric acid (H_2SO_4) treated rice husk increased compared to the raw rice husk, as consequences from the removal of the inorganic compounds such as carbonate and silica from the surface of adsorbent. Moreover,

purposely for dye removal, the enhancement of adsorption capacity of acid treated rice husk might also be because of protonation of the adsorbent surface. The surface became positively charged and electrostatic attraction developed between positively charged surface and negatively charged dye molecule which can further increase the amount of dye adsorbed. Common acids used for the purpose of chemical treatment of rice husk are hydrochloric acid (HCl), sulphuric acid (H₂SO₄) and nitric acid (HNO₃). As a conclusion, treatment with acids generally creates higher specific surface area and micropores area of rice husk adsorbent compared to non-activated adsorbent.

Objective:

- i) To check the feasibility of use of Rice husk and chemically modified rice husk.
- ii) Comparison of efficiency of both these adsorbents.
- iii) Treatment with Both husk at room temperature for contact duration 120 minutes.
- iv) Study of Removal of organic matter by adsorption techniques isotherm & reduction of BOD, COD content

Methodology:

- Step no 1 – collection of Sugar industry waste water sample.
- Step no 2 – to check actual quality of various parameters like pH, Conductance, Hardness, Alkalinity, Chloride, COD, BOD
- Step no 3- Preparation of adsorbent - Rice Husk- collection, Grinding, sieving, washing, drying
- Step no 4 - Measurement of particle size
- Step no 5 - Chemical activation of raw rice husk by 1% H₂SO₄
- Step no 6- treatment with bio-adsorbent –Rice Husk and Chemically modified rice husk with particle size 500 μm to Sugar industry waste water
- Step no 7- testing of treated Sugar industry waste water for parameter COD
- Step no 8- comparison of treated waste water with untreated waste water.
- Step no 9- graphical analysis of results.

Present study discusses the use of rice husk and chemically modified rice husk as an adsorbent for the removal of organic contamination present in the form of Chemical oxygen demand (COD) from sugar industry waste water. The method adopted for COD determination is Dichromate reflux method (11).

Results and Discussion:

Freundlich Isotherm:

$$\log x/m = \log K + 1/n \log C_{eq}$$

Linear plot of $\log C_{eq}$ Vs $\log x/m$ (COD and BOD) for rice husk suggests the applicability of this isotherm and indicate a monolayer coverage of the adsorbate on the outer surface of the adsorbent. - The steep slope indicates high adsorptive intensity at high equilibrium concentration that rapidly diminished at lower equilibrium concentration covered by the isotherm. - As Freundlich equation indicates the adsorptive capacity x/m is a function of the equilibrium concentration of the solute. Therefore, higher capacity is obtained at higher equilibrium concentrations.

Langmuir isotherm:

The plot of $1/C_{eq} \times 10^3$ and $1/q_e \times 10^2$ is linear confirms applicability of Langmuir isotherm for COD and BOD -Langmuir isotherm is a plot of the amount of impurity adsorbed by rice husk against the amount of impurity that remains in solution. It is a preliminary test to check the efficiency of particular material. -Langmuir's model is a 'Ideal localized monolayer model' according to which:

- ✓ The molecules are adsorbed at definite sites on the surface of the adsorbent.
- ✓ Each site can accommodate only one molecule (monolayer).
- ✓ The area of each site is a fixed quantity determine solely by the geometry of the surface.
- ✓ The adsorption energy is the same at all the sites.
- ✓ Such behavior on the basis of kinetic consideration, presuming that the adsorbed molecules cannot migrate across the surface of the interact with another neighboring molecules can be mathematically expressed as under

$$1/q_e = 1/\Theta_0 b \times 1/C_{eq} + 1/\Theta_0$$

The maximum COD removal is found at 40gm/L of Row Rice Husk and Chemically Modified Rice Husk concentration i.e. COD upto 59.077 % (rice husk) and 73.743% (modified rice husk).

Langmuir constant are the measure of maximum adsorption capacity. The value of the Langmuir parameters with correlation coefficient were computed from the intercept and the slope well fitted to Langmuir plot. It is clear from table that chemically modified rice husk is more efficient for removal of organics.

A wide range of agricultural products are used as adsorbent for removal of various organic and inorganic compounds because of their strong properties and characteristics of sorption

The potential of rice husk application for wastewater treatment should be highlighted due to its special and exceptional features as adsorbent. Specifically, rice husk has granular structure as well as insoluble in water. Moreover, it also has remarkable chemical stability and high mechanical strength. The most significant characteristics of rice husk is regarding to its local

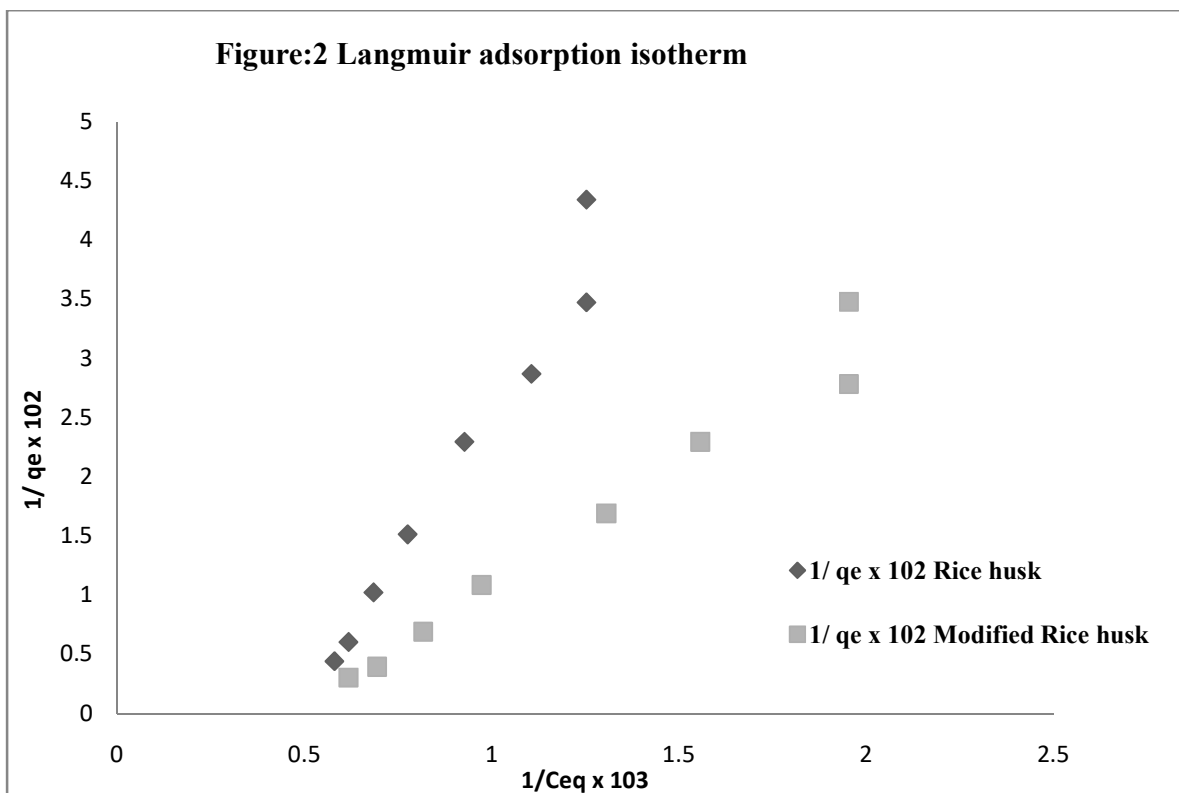
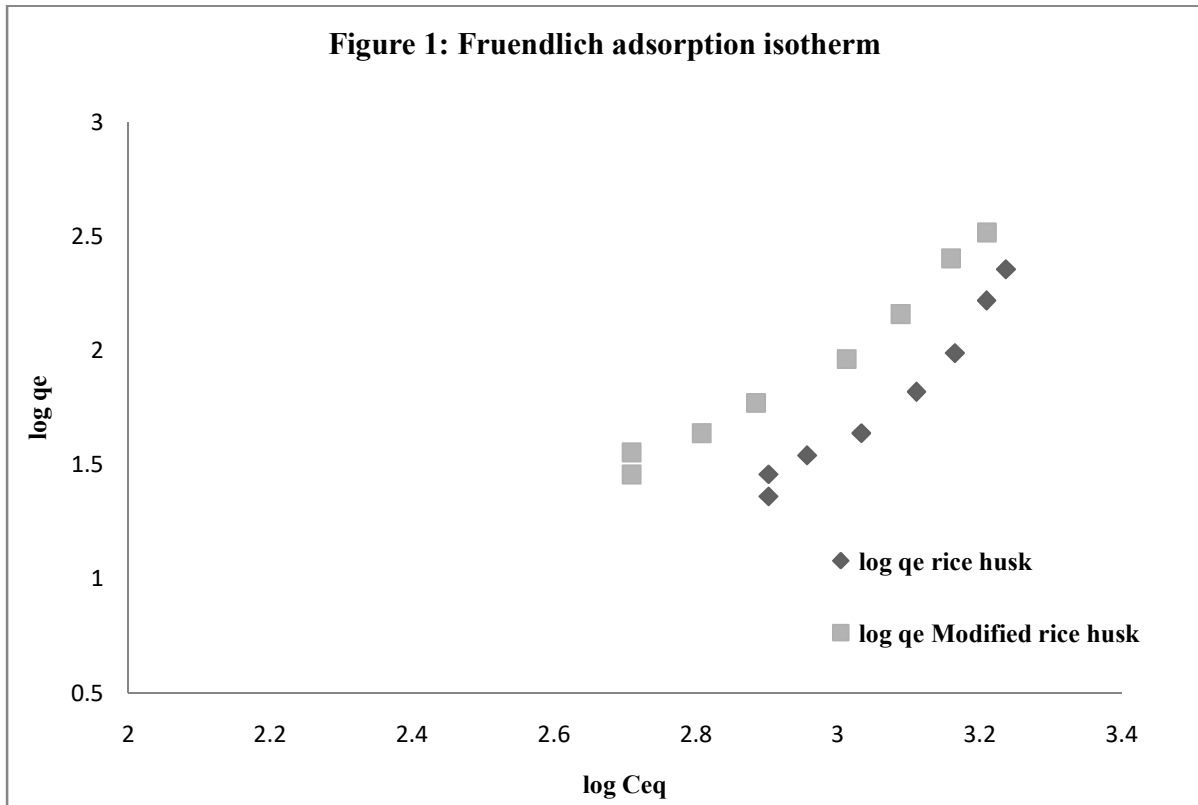
availability at almost no cost. Hence, there is no need to regenerated spent rice husk due to its low production costs. Moreover, rice husk is also tough and woody in nature, as well as poses abrasive inherent resistance behaviour. Other than that, rice husk also rich of silica – cellulose structural arrangement, which make it as a good adsorbent, compared to other agricultural wastes. This review will focus on nature of adsorption studies for heavy metals, dyes, surfactants, and organic compounds removal using rice husk. It also includes the knowledge facts on modification techniques of rice husk that are commonly employed by previous researchers. The physical treatment enables moisture loss as well as lignin decomposition of rice husk. On top of that, the treatment of rice husk by physical treatment also reduced the content of hemicellulose, lignin and cellulose crystallinity which leads to increase the specific surface area compared to raw rice husk.

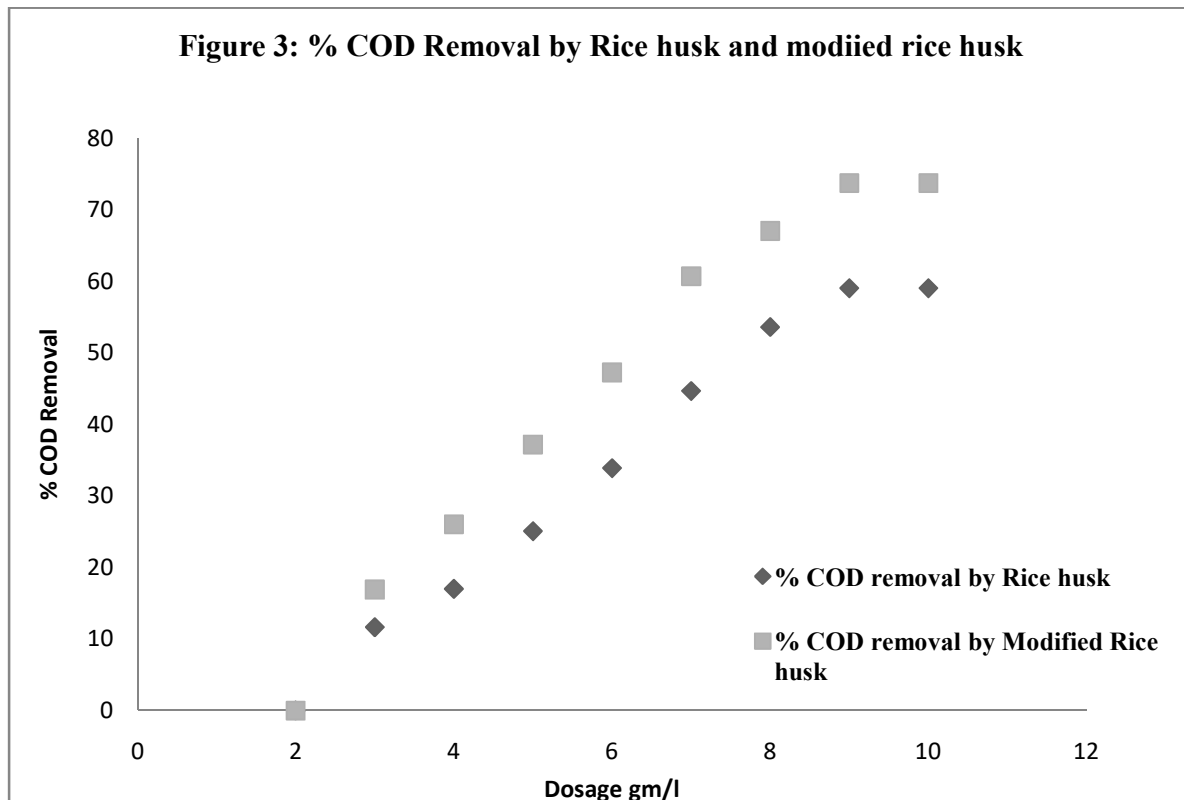
Conclusion:

- The final combined waste water of Sugar manufacturing unit is highly polluted having high COD and BOD.
- At room temperature Row Rice Husk and Chemically Modified Rice Husk work as an adsorbent and follow Freundlich and Langmuir isotherm models for COD removal. The results give straight line which confirms the applicability of isotherms.
- The maximum COD removal is found at 40gm/L of Row Rice Husk and Chemically Modified Rice Husk concentration i.e. COD upto 59.077 % (rice husk) and 73.743% (modified rice husk).

Fruendlich Langmuir adsorption isotherm parameter for Row rice husk and Chemically modified rice husk

Row Rice husk				Chemically Modified Rice husk			
Freundlich parameters		Langmuir parameters		Freundlich parameters		Langmuir parameters	
slope	0.3638	slope	0.1923	slope	0.4931	slope	0.4560
intercept	2.57	intercept	0.48	intercept	2.22	intercept	0.5
n	2.7487	θ	2.0833	n	2.0281	θ	2
k	560.64	b	0.0923	k	106.70	b	0.2280
R²	0.9543	R²	0.9674	R²	0.9733	R²	0.974





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