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Synthesis and Technological Application of Agro-Waste Composites for Treatment of Textile Waste Water

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***Abstract* – The untreated dyes released into the water reservoirs pose a toxic effect on the agricultural land through irrigation. Pakistan's economy is agro based demanding best quality product yield. However, the large consumption of rice in the country also produces waste (husk). It is either thrown or used as animal fodder.**

The present investigation is an endeavor to offer technological application of Rice Husk composite for treatment of azodyes (Congo red, Crystal violet, Methyl orange) from industrial effluents. For this purpose rice husk was modified with saturated (stearic) and unsaturated (oleic) fatty acids and applied as adsorbent in batch mode. Adsorption mechanism was accessed on the basis of varying adsorbent dose and adsorbate concentration for optimization of working parameters. The synthesized composite was characterized using FTIR, SEM-EDX, TGA and UV-Vis spectroscopy. FTIR spectrum showed sharp peak of esters (1700cm-1 - 1715cm-1) indicating modification due to fatty acids. It also suggests that binding of rice husk is through this ester linkage.

Adsorption experiments analyzes the increased removal efficiency of rice husk composites for dye, showing removal of 81% and 77% on oleic and stearic acid modification, respectively. An instantaneous adsorption-desorption hysteresis loop was attained in 20 minutes and 35 minutes under optimum conditions. Comparison among adsorbent composites for efficiency removal of azodyes showed that congo red dye removed more efficiently from industrial waste water as compared to other dyes. % Removal trend observed for azodyes was: congo red > crystal violet > methyl orange.

The present study concludes economical green synthesis of agro based composites and recommends its application for in-situ and ex-situ removal of azodyes from water reservoirs.

***Keywords* – Rice Husk, Free Fatty Acids, Adsorption, Congo Red, Methyl Orange, Crystal Violet.**

I. Introduction

Extraction of fatty acids from spent frying oil can be both by physical and chemical methods. Adsorption is physical process which can be used as an efficient process for removal of free fatty acids form spent vegetable oil (Baptiste et al,2013). Adsorpion process is not only less time consuming process but also lowers energy requirements as compared to extraction, esterification, distillation or such other chemical methods (Ilgen, 2014).

Industrialization is leading towards more pollution and toxicity. Our country is one of those who is confronting these pollution problems because Pakistan is the seventh most populous country of the world, having a population of more than 180 million. It is developing country with an increasing population density. In order to develop its economy, Pakistan requires establishment of many new industries. In 20^{th} century, all water bodies were being polluted due to unplanned industrial growth in different areas of Pakistan. In discriminate dumping of waste (solid and liquid) from different industrial units is the main cause behind pollution. Level of heavy metals, organic dyes and persistant organic pollutants (POP's) is increasing in water bodies and in environment. Law reinforcement for various industries to treat these contaminants is necessary.

Agricultural waste (AW) constitutes about 30% of overall agricultural productivity. Cellulose present in agricultural wastes shows potential of biosorption. AW materials (rice husk, rice bran, saw dust, eucalyptus peels, coconut husk, coconut shell fibre, bagasse, walnut peel, peanut hull, grams husk, netmug fibres, barks husk, barley husk, wheat husk, wheat bran hazelnut shell.waste tea leaves, jatropha plant ,fruits peel) are very good adsorbents and can play very important role in reducing pollution from the environment by removing heavy metals,dyes , persistant organic pollutants etc (Farook & Ravendran,2007; Bera et al,2004,Liu et al,2009).

Han et al., (2008) used ricehusk for removal of congo red from aqueous solution using column code. Parameters of initial pH, induced concentration, flow rate and existing salt were also studied. It was concluded that optimum concentration. Hameed et al, 2009 have synthesized a low cost pineapple stem (as an adsorbent) for the removal of cationic dye (methylene blue) from aqueous solutions.

Present study was performed in order to design such AW composites which are environmental friendly and will play role in removing azodyes from waste water. The green objective was to convert this load into useful commodity. For this purpose, an attempt was made to prepare composite of raw source with known fatty acids of waste oil. The composite was also applied as adsorbent.

II. Material and Methods

Raw material (rice husk) was collected from the local market. It was washed thoroughly, oven dried and crushed to sieve through 150 µm (100 mesh). The dried material (100 mg) was subjected to Sodium dodecyl sulfate (0.5 ppm, 10 ml) aqueous solution and acetic acid (10ml) for fuctionalization of biomaterial. The mixture was stirred for 4 hour at rotary shaker for homogenized mixing. Composites of synthesized biomaterials were prepared by addition of 10 ml fatty acids (stearic acid, oleic acid) (10 ml) into ricehusk. The mixture was subjected to reheating (50^0C) under stirring for 4 hours, filtered, washed repeatedly with ethanol to remove unreacted fatty acids.

Two newly synthesized biocomposites were coded as RFS (Rice husk functionalized Stearic acid) and RFO (Rice husk functionalized Oleic acid) respectively.

FTIR, TGA-DTA and SEM analysis were performed for confirmation of biocomposites formation.

III. Results and Discussion

3.1. FTIR Characterization

The raw rice husk sample exhibited -CH stretching vibrations with high percent transmittance at 2850 cm^{-1} However, rice husk modified with stearic acid (RF1, RFS)

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showed peaks in the same region but of low transmittance. A peculiar peak at 1713 cm^{-1} and 1708cm^{-1} confirms the incorporation of oleic acid (RFO) and stearic acid (RFS), respectively in synthesized biomaterials (Vlaev, et al, 2009). This peak is characteristic of unsaturated esters, that are expected to develop as a result of reaction between fatty acid and –OH groups. Literature also validates presence of unsaturated esters or –C=O group (ketones and aldehyde) in the range of 1710- 1665/cm.

3.2. TGA-DTA analysis

TGA/DTA analysis was also done in order to make a comparison in weight loss changes in samples by modification with fatty acids. In case of ricehusk composites three steps of decomposition were observed.Temperature given was upto 650^{0}C.It can be seen that agro waste composites(RFS,RFO) showed quite resemblance with eachother in TGA/DTA curves.These results are supported by (Gai et al,2013).On modification of rice husk with fatty acids a massive weight loss was observed in comparison to raw rice husk.Rice husk showed second step thermal decomposition within temperature range of 175-400^{0}C.Which was reduced to 375^{0}C in case of RFO and to 300^{0}C in case of RFS.Residual content was also measured, as followed by (Kumar et al,2008).Overall residue calculated was more for raw ricehusk(36%) than oleic acid modified rice husk(27%) and than for stearic acid modified rice husk(4%).

It can be suggested that stearic acid modified biomaterials (RFS) are readily affected by temperature and undergo pyrolysis at earlier stages than that of oleic acid modified biomaterial composites(RFO).It can be attributed to long carbon chain of stearic acid (C18) which undergo rapid weight loss with very less residual content as compared to short chain unsaturated compound(C14).

3.3. Scanning Electron Microscopy (SEM)

Each of the synthesized composites was scanned for electron micrographs to determine the surface morphology and particle size. The composites of Rice Husk scanned under electron microscope reveals surface characteristics in detail. The stacking of crystallites into ordered longitudinal channels of Rice Husk is highly enhanced in modified composite. It can be seen that one stack of crystal is distinctive from other with some wider and deep crevices as connecting tunnel. This tunnel is expected to provide path for adsorptive removal of pollutants in batch adsorption experiments.

The synthesized composites from agricultural waste of biomaterials are applied as adsorbents for in-situ and ex-situ remediation of selected azo-dyes. The removal efficiency was measured at varying parameters of adsorbent dose and adsorbate concentration.

3.4.1 Effect of Time

The impact of time on adsorption was significant. A general decreasing and increasing trend was noted in a single batch experiment. The present study results are comparable to (Annadurai et al, 2002) where rate of adsorption is found to increase upto 10 minutes. The optimum removal (>75%) attained by modified composite with stearic acid (RFS). oleic functionalized rice husk (RFO) is proven to be a better adsorbent for Congo red. This change may be attributed to higher silica content in rice husk, offering more binding potential due to enhanced cation exchange capacity.

Removal of basic dye was also assessed on the synthesized composites. The sequence followed by set of adsorbents followed the trend, i.e., base > stearic > oleic. It is interesting to note that oleic functionalized composites have a better retention capacity for crystal violet (407.979 g/mol) than Congo red (696.66 g/mol). It is related to the fact that basic dye is retained to sufficient extent on short carbon chains (oleic acid). Further, the lower molecular mass of crystal violet facilitates its diffusion into the pores of matrix. See fig 1 (a-c)

The removal of acid-base indicator (methyl orange) reveals interesting adsorption trend. The functionalization of oleic acids shows more adsorption than stearic modification of composites. It can also be drawn that raw rice husk is poor adsorbent, with comparable percentage removal (less than 40%) while cation exchange capacity is more in modified rice husk composites for fatty acids.

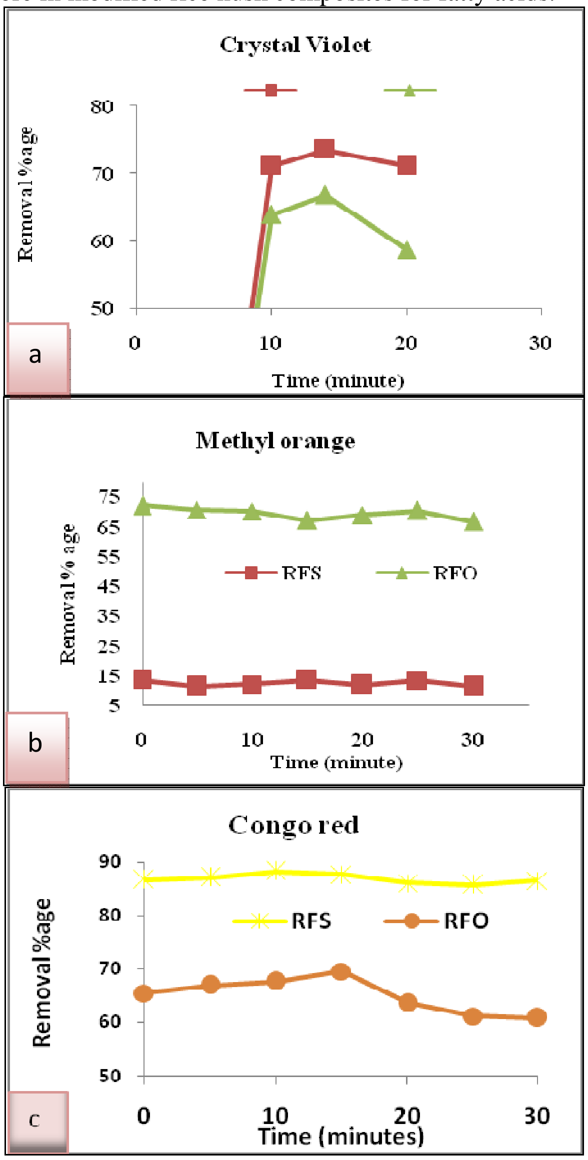

Fig.1. (a) Effect of time on removal of crystal violet (b)methyl orange (c) Congo red

3.4.2. Effect of dose

The removal of probable carcinogenic dyes is attempted on the composites synthesized from natural waste. A range of dosages was subjected to different dyes. The results (shown in Figure) depict 15mg/Kg to be the optimum dose for basic dyes. On the other hand, acid base indicator removes optimally on 10mg/Kg. However, no further significant increase is noted for increased adsorbent dose, that may be due to agglomeration of sites (Alijebori et al, 2012) or overcrowding of adsorbent particles (Garg et al,2003).

Congo red exhibits unique and universally suited for a wide range of doses, showing comparable removal potential at different doses.

A further probe into the adsorption process reveals that Rice Husk composite is relatively better adsorbent for the removal of acidic and basic dyes as compared to raw rice husk.

3.4.3. Effect of Concentration

The aqueous solution of dyes of different strengths (0.01mg/L, 0.03mg/L and 0.05mg/L) was induced to synthesized composites, under optimum operating parameters. A general increase in uptake is found associated at higher concentrations. It also suggests that in order to determine the optimum concentration, higher strengths need to be induced.

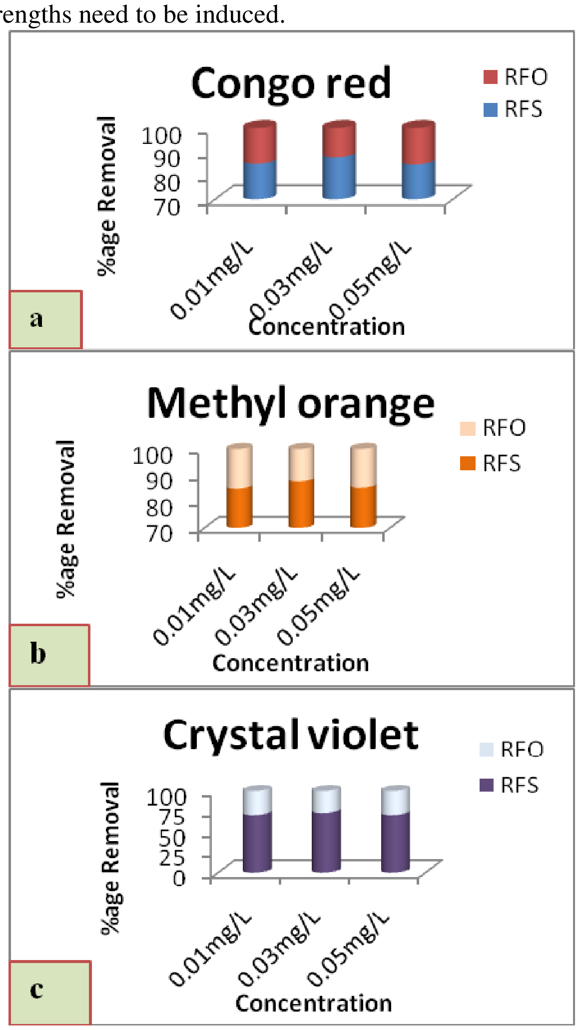

Fig.2. (a) Effect of dose on % removal of congo red (b) methyl orange (c) crystal violet

The marginal difference in strength may speak for the reason. The optimal removal of Congo red on two rice husk composites is found to be comparable (94% and 98%). The present study results are supported by a number of researcher (Mittal et al, 2014., Mohanty et al, 2006., Haque et al, 2011) showing the efficient removal of basic dye in comparison to other.

The quantification of crystal violet demonstrates more uptake on coconut fiber composite. However, optimal concentration of dye for these adsorbents cannot be precisely defined and need to be extended further investigation. On the contrary, 0.03 mg/L is the optimally determined strength for rice husk composites.

Methyl orange removal on two sets of adsorbents follow the same trend as explained for crystal violet. This similarity in behavior of two dyes might draw the attention of the researcher, that methyl orange at the particular strength (0.03mg/L) occupies the basic form as in case of basic dye (crystal violet). See fig 2(a-c).

IV. Conclusion

Successful synthesis of fatty acids modified composites was confirmed by FTIR, SEM and EDX. The newly synthesized biomaterial composites also showed its positive potential in removal of azodyes (Congo red, methyl orange, crystal violet) from waste water in trend followed as: congo red>methyl orange>crystal violet.

Modified bio-composites with fatty acids (stearic, oleic) separately had shown more good adsorption behavior due to hydrophobic interactions between adsorbate and adsorbent as compared to raw rice husk.

Kinetics results conclude that Pseudo second order, Freundlich, Langmuir and Temkin Isotherms were best fit on experimental data.

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