PLANT WASTE UTILIZATION AS ECOFRIENDLY SORBENTS FOR REMOVAL OF REACTIVE DYES FROM WASTEWATER

A. Shahzadi[1], S. Nosheen*[2], S.Kiran[3], S.Riaz[4], T.A.Mughal[4] and L.Shahid[5]

[1-6] Department of Environmental Science, Lahore College for Women University, Lahore
[3]Department of Applied Chemistry, Government College University, Faisalabad
Corresponding author's Email: sofia.nosheen@lcwu.edu.pk

ABSTRACT: Present work was focused on the removal of reactive dyes involving management of agro-waste (chickpea pods, pea pods, potato peels, onion peels and eucalyptus leaves) directly and their conversion to green biosorbents. Dye removal efficiency was monitored by UV-Visible spectrophotometer and the adsorption process was evaluated by scanning electron microscopy (SEM) as well. Maximum dye removal (99%) was obtained from chickpea and pea pods while as a natural biosrbents they remove selected dye up to 24.5% and 28.5% respectively. Continuous monitoring showed that decolorization efficiency of selected biosorbent has a direct relationship with contact time. Synergistic effect was observed between green biosorbent and chitosan. Overall findings of present work confirmed that activated carbon of chickpea and pea pods could be an effective and environment benign (green) adsorbent to remove reactive dyes from industrial effluents.

Keywords: Agro-waste, bio-sorbent, Activated carbon, Reactive dye Decolorization efficiency.

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INTRODUCTION

Water scarcity issues are rising day by day because of population explosion which is expected to be 9.3 billion. This is because of waste entering through various vicinities like paper, textile, cosmetics and food industries that are posing serious environmental concerns (Markham, 2019). Each year more than 100, 000 dyes are produced commercially (estimated 7x 10^5 tons per year) (Katheresan *et al.,* 2018. Dyes present in textile water are more injurious to environmental health due to degradation resistance, high visibility and toxic impacts (Asghar *et al*., 2015). Most of dyes are visible even in their low concentration and affect light and oxygen penetration disturbing aquatic life (Lellis *et al.,* 2019). Additionally dyes are also very toxic to human health as they may cause cancer, skin irritation, allergies, tumors, mutations and heart effects (Tang *et al.*, 2018). There are several methods to remove dyes like chemical treatment, ozonation process, electrochemical destruction, oxidative stress, ion exchange, electrochemical, irradiation, membrane filtration, coagulation, biological treatment and biosorption (Azari *et al.,* 2020). Biosorption is considered to be cost effective, competitive and easy approach. In this process a bio-sorbent (any biological matrix) interact with sorbate (a molecular ion, molecule, etc.) which result in accumulation of sorbate-biosorbent interface and consequently reduce sorbent concentration in solution (Robalds *et al.,* 2016).

Biosorption is divided in several categories like adsorption, ion exchange, surface complexation, absorption and precipitation. This is living and dead biomass property (San Keskin *et al.*, 2018). Agricultural waste contains some basic constituents like starch, sugar, polysaccharides, lipids, proteins, cellulose, lignin and pigments. They have different functional groups like hydroxyl, sulfhydryl, amino group and carboxyl. These functional groups have the ability to bind with sorbate molecules and ions (Li *et al.,* 2012; Huang and Zhu, 2013). They are rich in carbon content that can be converted into activated carbon/ charcoal which is potential adsorbent in removing pollutants (Wong *et al.,* 2018).

Pakistan is facing water scarcity and large amount of industrial effluents poses great threat to ecosystem. On the other hand, improper management of agricultural waste is another alarming situation (Qureshi and Ashraf, 2019). The objective of our study is to synthesize bio-sorbent based on agro-waste and to apply it to treat waste water as eco-friendly and sustainable solution.

MATERIALS AND METHODS

Waste plant materials (onion peels, potatoes peel, eucalyptus leaves, pea and chick pea) were collected from household waste and from local vegetable and fruit markets of Lahore Pakistan. Dye was provided by Sandal dyestuff (PVT) limited. After removal of any dust/ sand physically (by drying, sieving or grinding), all materials were stored in air tight jars.

Bio-adsorption: In each experiment pre-weighed (0.5 mg, 1mg, 10mg, 0.5g, 1g and 2g) amount of bio-adsorbent were added to dye solution having various concentration. After specific time interval the samples were filtered. The filtrates were analyzed by UV-Visible spectro-photometer at 493nm wavelength and different factors like temperature, agitation, concentration, contact time were investigated.

Preparation of activated carbon: Peas and chickpea waste was used to prepare activated carbon. Carbonization procedures were used as described by Sundari and Balasubramaniam, (2014).

Direct pyrolysis: The dried peas and chickpea pods were carbonized at 400°C into well powder form and then activated at 800°C for 10 min. After activation process, activated carbon was washed with distilled water consequently and was dried to obtain thermal activated carbon.

Carbonization with H_3PO_4: The dried peas and chick pea pods were soaked in a 30% boiling solution of H_3PO_4 for 2 hours and soaked for 24 hours in same solution. Consequently extra solution was evaporated and air dried. The remnant was carbonized at 400°C in muffle furnace. Dried matter was powdered and activated at 800°C in muffle furnace for 10 minutes. Activated carbon was washed with water to remove acid and dried into powdered form.

Preparation of composite of Chitosan and natural Bio-adsorbents for removal of reactive dye: Composite of Chitosan and natural bio-adsorbent were prepared in different ratio (1:1 CH:CP, 2:4 CH:CP& 1:1 CH:P, 2:4 CH:P) in order to evaluate the removal of reactive dyes.

RESULTS AND DISCUSSION

The percentage dye removal was recorded on the basis of decrease in absorbance as calculated by UV-Visible spectroscopy. Results shown in Figure- (1&2) indicated that removal of dye using agro-waste based bio-adsorbents under static, shaking and heating conditions at different dye concentrations. Maximum removal of dye was shown by pea and chick pea pods was up to 28.5% (50ppm, under heating condition) and 24.5% (at 50ppm, under static condition) respectively while the other green adsorbents (onion peels, potato peels and eucalyptus leaves) slightly removed the dye as natural adsorbent without any chemical treatment. Further experiments were carried out with only biosorbent from chickpea and pea pods. Agitation affected bio-adsorbent process by increasing the optimum shaking rate that increased adsorption (Subki *et al.,* 2019) but the present study showed that there were no significant changes occurred while performing experiment in case of static and shaking condition (Figure-1&2).

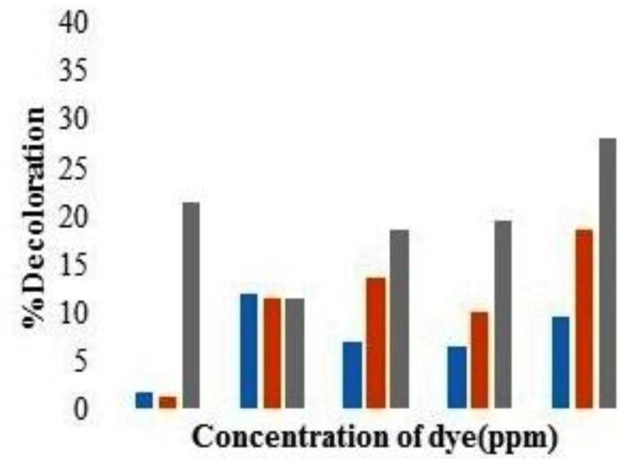

Figure- 1: Percent discoloration of reactive dye by natural adsorbents pea under static, shaking and heating conditions

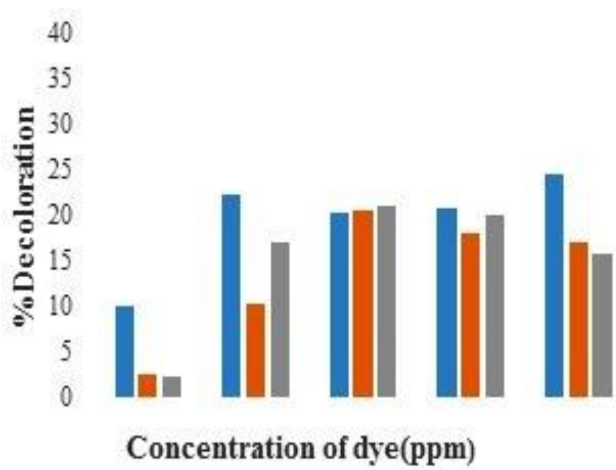

Figure- 2: Percent discoloration of Reactive dye by natural adsorbents chickpea under static, shaking and heating conditions.

The effect of temperature shows that there are two behaviors of bio-adsorbate after increasing temperature in one side there is increase in percent discoloration of dye up to 28.5% because increase in temperature effect the solubility and chemical properties of bio-sorbent while on the other hand some green bio-sorbents show decreasing value of color removal this indicate that the bio-sorption process become exothermic in nature that also reported in literature (Mahmoud *et al.,* 2016).

Contact time is another important factor that significantly affect the biosorption process (Fig- 3) show the comparison that after increasing the contact time of bio-adsorbent Removal of reactive dye also increase up to 43% to 53% because particular time of contact is required to establish equilibrium between adsorbate and adsorbent that usually depends upon the nature and concentration of adsorbate also investigated in past (Subki*et al.,* 2019).

Agro-waste are rich in carbon content and offer significant potential to obtain porous bio-adsorbents. In this study Activated carbon prepared from peapods and chickpea pods proved excellent and effective low-cost replacement for non- renewable activated carbon and chitosan. Figure- 4 illustrated the removal of dye by activated carbon made from green bio-sorbents up to 99% obtained from two process direct pyrolysis and carbonization with H_3PO_4.

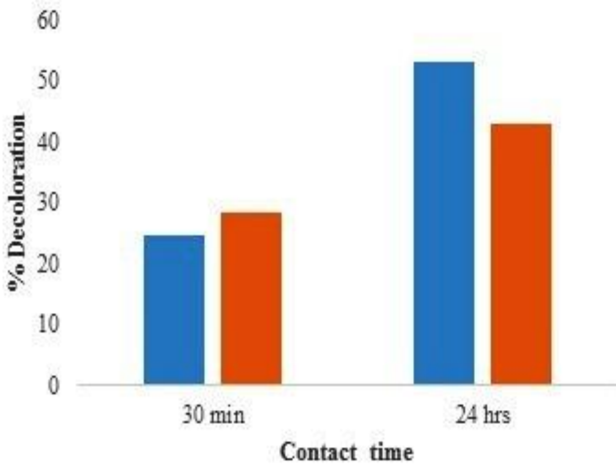

Figure- 3: Percent discoloration of Reactive dye by natural adsorbents pea and chickpea after increasing contact time

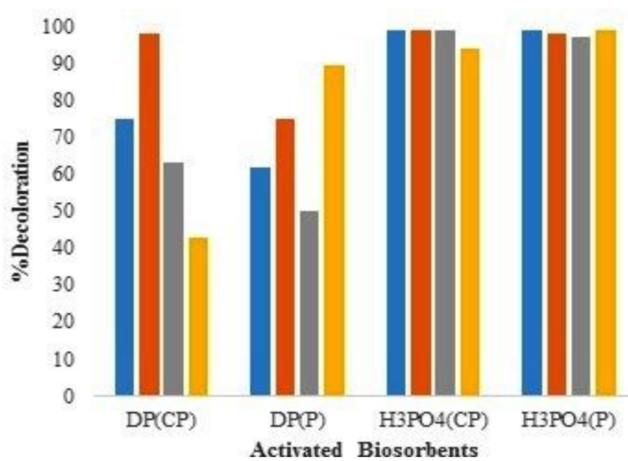

Figure- 4: Percent discoloration of Reactive dye by Activated carbon (Direct Pyrolysis and carbonization with H_3PO_4) of Green biosorbents (CP: chickpea, P: pea)

Dye removal efficiency of Reactive dye was checked from composite of Chitosan with natural bio-adsorbents (pea and chickpea pods).Result showed that the % discoloration of reactive dye was 32% under static condition at 50ppm(2:4 CH:CP) while the minimum removal was 8.3% at (room temperature +shaking) at 50ppm (1:1CH:CP) (Figure 5).On the other hand composite of natural bio-adsorbent pea and chitosan show 18% discoloration of dye at static 50ppm(2:4 CH:P) and RT+S 50ppm(1:1 CH:P) and the minimum dye removal was 4.4% at High (Temperature + Shaking), 50ppm (2:4 Ch:P) (Figure 6).

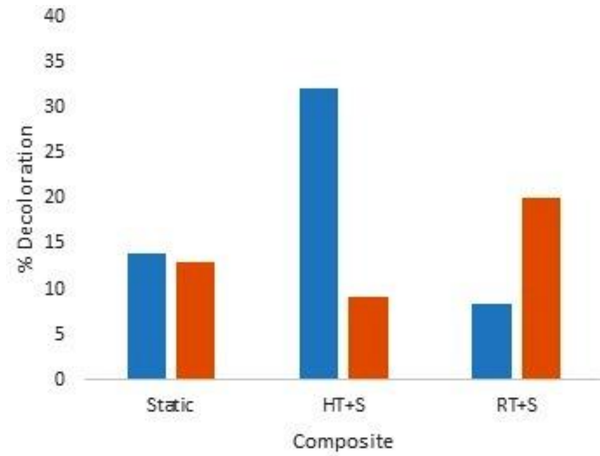

Figure- 5: Percent discoloration of Reactive dye by composite of Chitosan and chickpea (static, HT+S: high temperature + shaking, RT +S: room temperature +shaking) condition

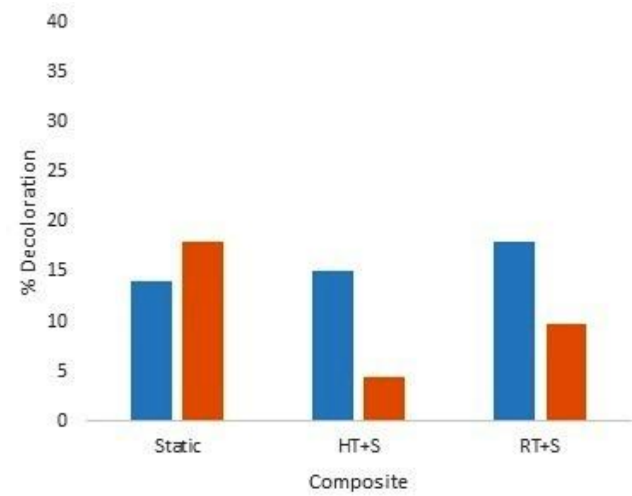

Fig 6 % Decoloration of Reactive dye by composite of Chitosan and pea (static, HT+S: high temperature + shaking, RT +S: room temperature + shaking) condition.

Characterization of bio-adsorbent: The surface structure and texture of adsorbent were characterized by Scanning electron microscopy represented in fig- 7and 8.

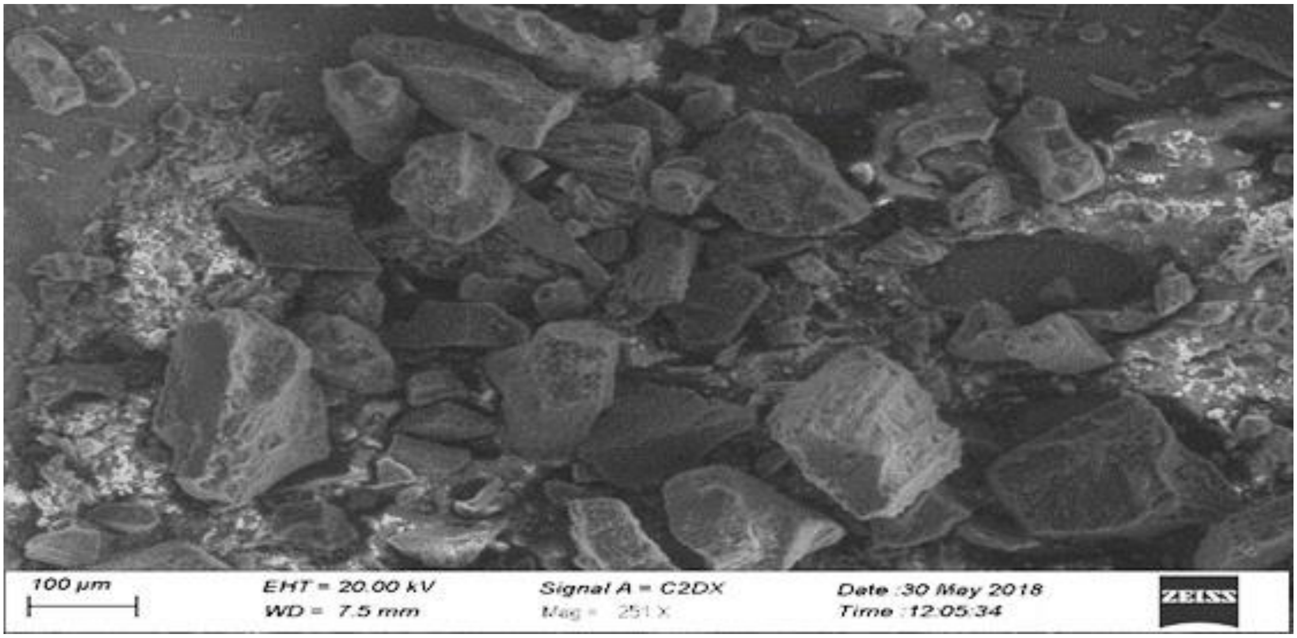

Figure- 7: SEM images of activated carbon before treatment

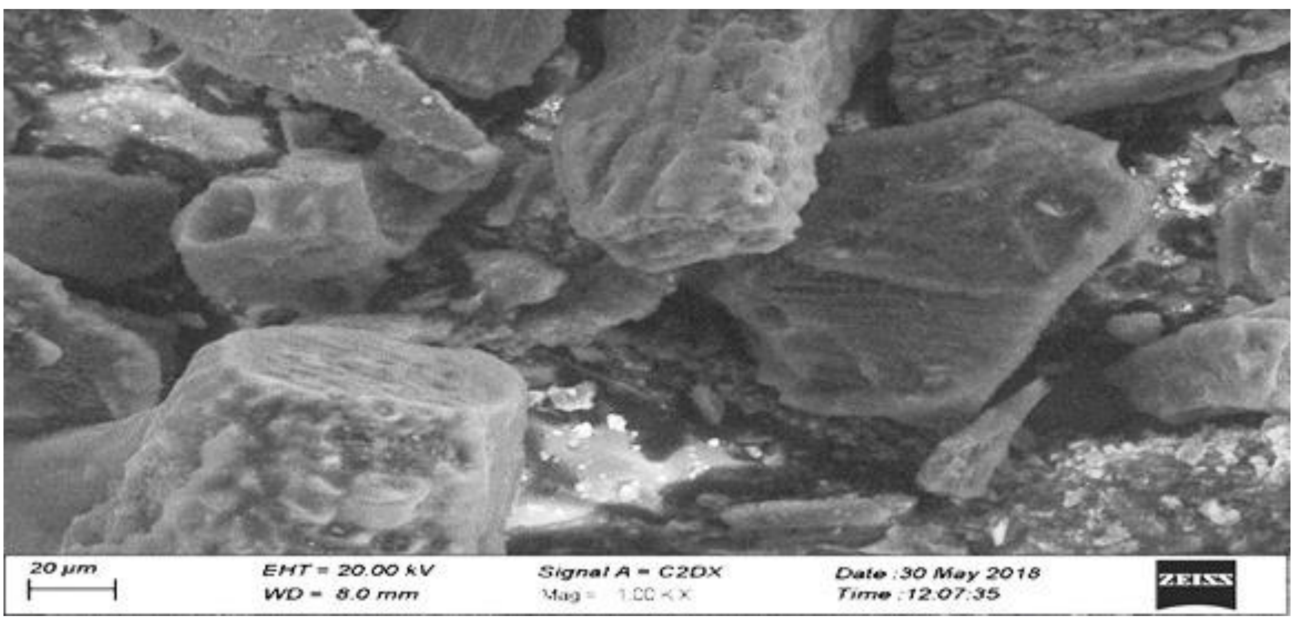

Figure- 8: SEM images of activated carbon after treatment loaded with Reactive dye

Conclusion: It was concluded that natural agro-waste present in large amount can be used as an effective measure for removal of reactive dyes. Activated carbon prepared from chickpea and pea pods by direct pyrolysis and carbonization with phosphoric acid showed better removal of reactive dye up to ninety-nine percent.

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