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Research Article

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Adsorption and reaction kinetics of tatrazine by using *Annona muricata* L seeds

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ABSTRACT

Adsorption of tartrazine by Annona muricata L seeds has been investigated. The experiment was done by batch system for examine the optimum conditions of dye adsorption. Effect pH, contact time, stirring rate, concentration and adsorbent dosage have been studied. Isotherm adsorption were measured experimentally. Maximum adsorption of dye was 23.6310 mg/g achieved at pH 2, contact time 120 minutes, stirring rate 100 rpm, initial concentration 600 mg/L and adsorbent dosage 0.1 g. Fourier Transform Infra-red spectroscopy was used for determination of functional group content in Annona muricata L. seeds. This spectrum indicated of hydroxyl group and carbonyl group as active site. The surface of Annona muricata L seed powder has porous and provide for dye uptake. Isotherm Langmuir and Freundlich model were indicated that the process adsorption was physic adsorption and adsorption process was pseudo-second order kinetic model with R^2 0.982.

Keywords: tartrazine, adsorption, *Annona muricata L* seeds, FTIR

INTRODUCTION

Various liquid dyes waste treatment have been developed. Among these physico-chemical methods like adsorption, electrochemical coagulation and photocatalytic decolourization. Among all these, adsorption is one ofthe methods, which is gaining attention becauseof its easy operations and versatility[1]. Biosorption is an alternative and eco-friendly way to overcome these pollutants. In spite of economic reason, utilization of agricultural by-product as biosorbent also reduces solid waste. Biosorbents from agricultural byproduct such asfeathers [1], fruits waste [2], coconut husks [3], mango seeds [4], moringa seeds[5], apricot seeds [6], *Eugenia jambolana* seeds [7] , and cocoa shell[8] were used to reduce dyes from waste water.

Annona muricata L seeds have been used for the removal of Pb, Cd, Zn, and Cu ion from wastewater [9]. Other seeds also used to remove dyes such as mango seed to victazol orange 3R[4], moringa seeds to orange 7 [5], apricot seeds to brown VBR [6], *Eugenia jambolana* seeds to acid yellow [7], *Annona squmosa* to methyl red [8], ashoka seeds to methylen blue [16], tamarind seed to crystal violet [17]. This study investigate the use of *Annona muricata L* seeds for the removal of tartrazinedye present in industrial wastewater.

Tartrazine is widely used as foods, drinks and cosmetics colorant. Tartrazine is carcinogenic and cause allergic with molecular formula $C_{16}H_9N_4Na_3O_9S_2$water soluble and mass of molecule is 534.4 g/mol. It is found in certain brands of fruit squash, fruit cordial, coloured fizzy drinks, instant puddings, cake mixes, custard powder, soups, sauces, ice cream, icelollies, sweets, chewing gum, marzipan, jam, jelly, marmalade, mustard, yoghurt and many convenience foods together with glycerine, lemon and honey products. It is cheaper than betacarotene and therefore used as an alternative to beta carotene to achieve similar colour. Tartrazine is also reputed to catalyze hyperactivity and other behavioral problems, asthma, migranes, thyroid cancer, etc. Because of its hazardous health effects, foods and drinks

containing Tartrazine are avoided[1]. Tartrazine adsorption have been carried using hen feather[1], melamine-formaldehyde-tartaric acid resin[10], chitosan bead[11], coconut husks[3], fly ash [12], saw dust [13], and biomass such as fungus[14] and algae [15].

EXPERIMENTAL SECTION

In present work, the biosorption experiments were conducted by using standard stock solution (1000 mg/L) of tartrazine (E-Merck, Germany). Working standard solutions were prepared just before used by appropriate dilution of stock solution.

Seed preparation and characterization

Seedsof *Annona muricata L* (Annona muricata, L) were washed, dried, then ground with a crusher (Fritch, Germany). After milled, dried in oven (Memmert, Germany) at 60 °C for 1hour. Soaked for two hours with HCl 0.01M. Furthermore, pale colored powder was washed with distilled water and dried. Biosorbent is ready for used.

The dry powder was treated with 10 mL tartrazine 20 mg/L, shaked for 1 h with 100 rpm and then filtered. The filtrate was analyzed with spectrophotometer (Genesys 20ThermoScientific) to determine total amount of tartrazine was been adsorption at 427 nm. There are several parameters to be treated to get optimal condition of tartrazine adsorption with biomass.

The amount of adsorbed tartrazine per gram of the biomass (adsorption capacity, q) was obtained using the following equation [15] :

$$q = \frac{(C_o - C_e)V}{m} \quad \text{(eqn 1)}$$

whereC_o and C_e were initial and equilibrium concentration of tartrazine (mg/L), respectively; V was volume of tartrazine solution (L); m was amount of biomass (g).

RESULTS

Effect of pH on adsorption of tartrazine

pH plays an important role in the absorption of tartrazine by *Annona muricata L* seeds. pH will determine biosorbent surface charge, degree of ionization and dissociation of various functional groups of the active site of adsorbent [13]. Tartrazine adsorption process carried out at pH 1-8. Fig.1 shows the effect of pH on the absorption of tartrazine.

Adsorption capacity maximum of tartrazine 1.3586mg/g occurred at pH 2. Absorption capacity decreased from 1.0245 to 0.8795 at pH 3 to 4. Meanwhile at pH 1 competition between H^+ ions with tartrazine occur there by reducing absorption capacity.

Tartrazine absorption capacity decreased with increasing pH of the solution. This is due to the OH^- ion activity affected to surface charge of the biosorbent. Tartrazineis an anionic dye is negatively charged while dissociating thus biosorbent surface that contains OH^- ion decrease adsorption tartrazine. Susmita explained that by increasing the pH of the positive charge decreased adsorbent becomes negatively charged. This condition does not support the uptake of anionic dyes from the system and causing electrostaticr epulsion[13].

According to Mohammed A. Kassem et al. [19] increase of protonation due to neutralization of negative charge at the surface of the adsorbents, which facilitates diffusion and provides more active surface of the adsorbents, resulting thereby greater adsorption at their surfaces. The pH of solution controls the electrostatic interactions between the adsorbent and the adsorbate. A decrease in the percentage removal with increase in pH may be due to deprotonation, which retards the electrostatic forces between sorbent and sorbate that leads to reduced sorption capacity.

Previous research observed adsorption of tartrazine by hen feather achieved maximum capacity of adsorption at pH 2 [1]. Meanwhile Susmita *et al*[13] and Mohammed A. Kassem[19] observed adsorption of tartrazine by saw dust and activated charcoal obtained maximum capacity of adsorption at pH 3 and 1,5 respectively.

Effect on contact time on adsorption of tartrazine

Effect of contact time on the uptake tartrazine performed at a concentration of 20 mg/L with stirring rate of 100 rpm and pH 2. Biosorption process continues to increase with increasing contact time but slowly decreases after passing

optimum time. The optimum time for absorption tartrazine with *Annona muricata L* seeds is 120 minutes with the absorption capacity of 1.6537 mg/g. Fig.2illustrates the effect of contact time on the process of adsorption.

This is due to availability of vacant surface sites during the preliminary stage of adsorption, and after a certain time period the vacant sites get occupied by dye molecules which lead to create a repulsive force between the adsorbate on the adsorbent surface [13].

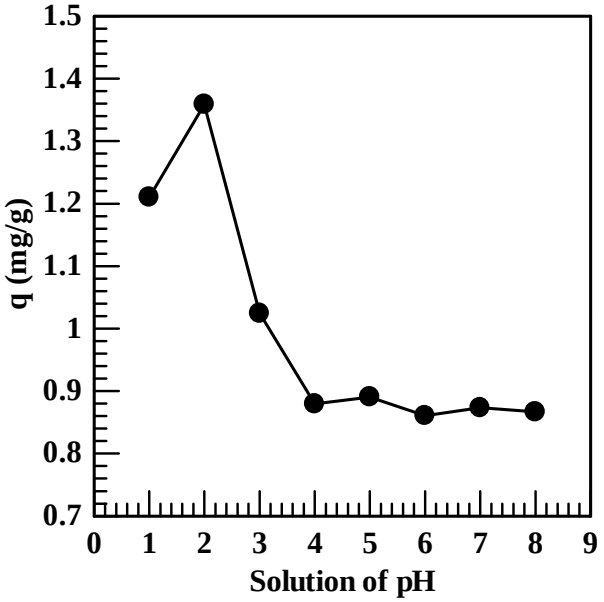

Fig.1. Effect of pH on tartrazine adsorption; concentration 20 mg/L; biosorbent mass 0.1 g; contact time 120 min; stirring rate 100 rpm

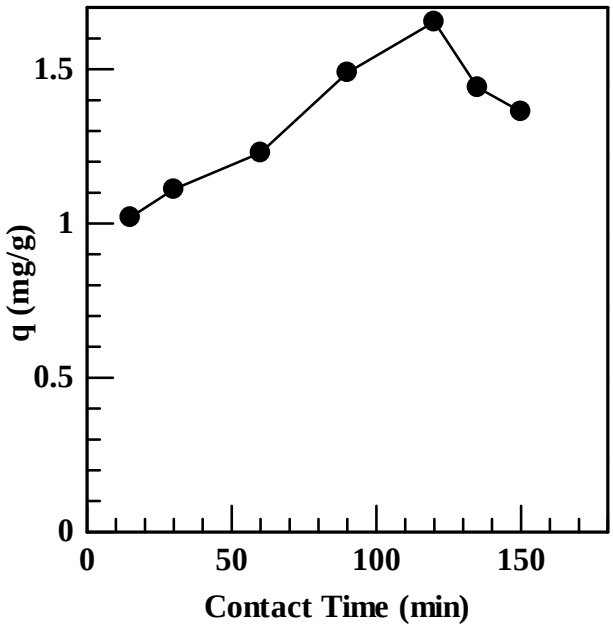

Fig.2.Effect of contact time on tartrazine adsorption, concentration 20 mg/L; pH 2; mass of biosorbent 0.1 g; Shaking speed 100 rpm

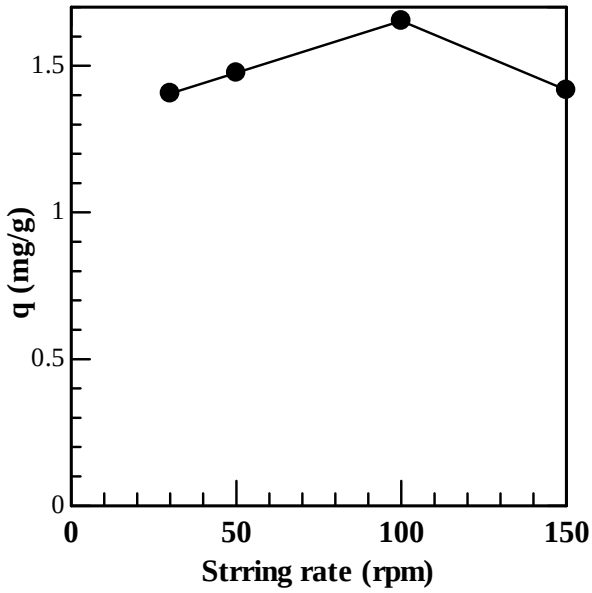

Fig.3. Effect of stirring rate on tartrazine adsorption,consentration 20 mg/L; pH 2; contact time 120 min; biosorbent mass 0.1 g

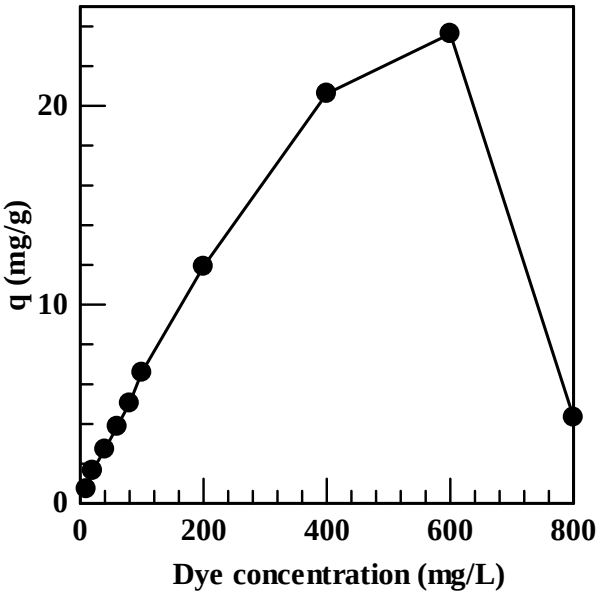

Fig. 4. Effect of concentration on tartrazine adsorption, pH 2; contact time 120 min; stirring rate 100 rpm; biosorbent mass 0.1 g

Susmita etal used saw dust to the absorption tartrazine obtain optimum contact time of 70 minutes [13]. Mohammed A. Kassemusing activated charcoal to adsorption tartrazine achieve optimum time of 90 minutes [19]. None the less Alok etal found that the absorption increases as contact time increase [1].

Effect of stirring rate on adsorption of tartrazine

Effect of stirring rate performed at pH 2with a contact time of 120 minutes. Stirring rate was varied from30 to150rpm. Effect of stirring rate on the adsorption process is shown in Fig.3.

Maximum adsorption of removal tartrazine obtained at 100rpm. Increase stirring rate adsorption capacity decrease due to rapid rotation caused dyes which have been bond to biomaterial regardless return increase absorbance capacity of adsorption decrease.

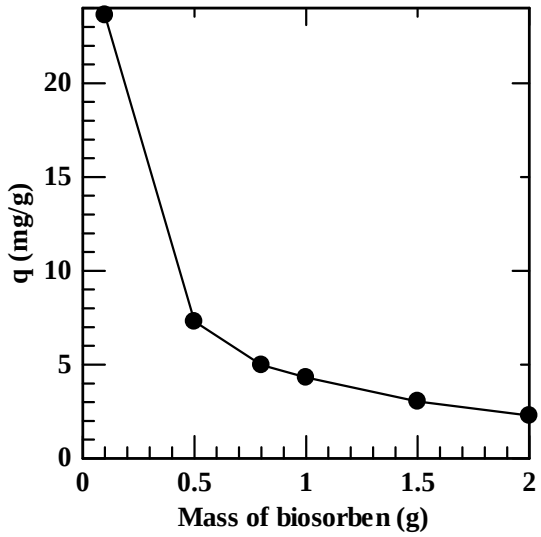

Fig. 5. Effect of adsorbent doses on tartrazine adsorption;concentration 600 mg/L; pH 2; contact time 120 min; stirring rate 100 rpm

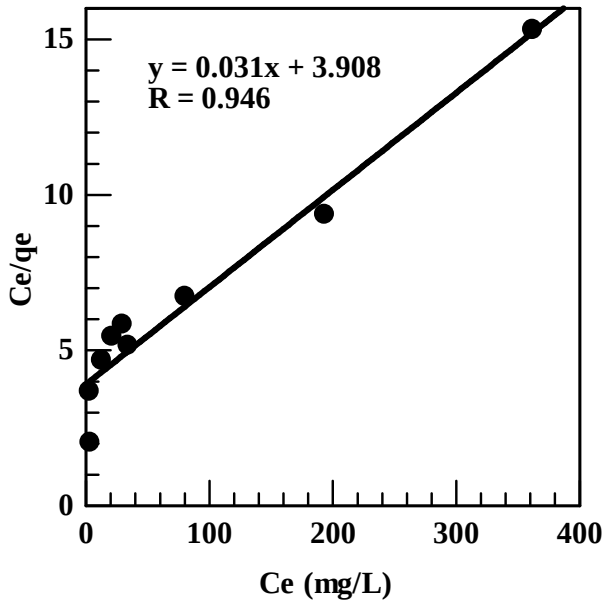

Fig.6. Langmuir isotherm for adsorption of tartrazine on to *Annona muricata L* seeds; data retrieved from Fig. 4 (10-600 mg/L)

Stirring effect on the distribution of the dye molecules in solution and the formation of a thin layer of dye molecules around the active sites on the surface of the biosorbent. With the increase of stirring rate, the efficiency of biosorption decreased because all sides have been actively used in the biosorption process [7]. At higher speeds the dye molecules do not have enough time to come into contact with the active sorbent. Mohammed A. Kassem obtain optimum stirring rate for adsorption of tartrazine with activated charcoal at 100rpm.

Effect of concentration on adsorption of tartrazine

Effect of concentration tested at pH 2 with a stirring rate of 100 rpm and contact time for 2hours. As a function of the concentration of biosorpi process shown inFig.4.

Fig. 4 shown optimum concentration on adsorption of tartrazin was 600 mg/L. Increase concentration of adsorbate capacity of adsorption decrease. Alok *etal* have been doing research on the absorption of tartrazine with hen feathers and obtain results that with increasing concentration absorption capacity increased[1]. Susmita Banerjee who were

investigating absorption of tartrazine with saw dust showed absorption capacity (q) continues to steadily increase with increasing concentration, but after reaching equilibrium sorption capacity decreased. This is may caused by the availability of vacant adsorbent surface in the early phase and after a certain time the vacancy is occupied by adsorbate molecules that cause repulsion between adsorbate molecules and adsorbent [13]. Himanshu Patel *etal* mentioned certain mass of adsorbent can only absorba certain amount of adsorbate. Therefore, the more concentrated the smaller adsorbate volume which could be purified by acertain amount of adsorbent mass [17].

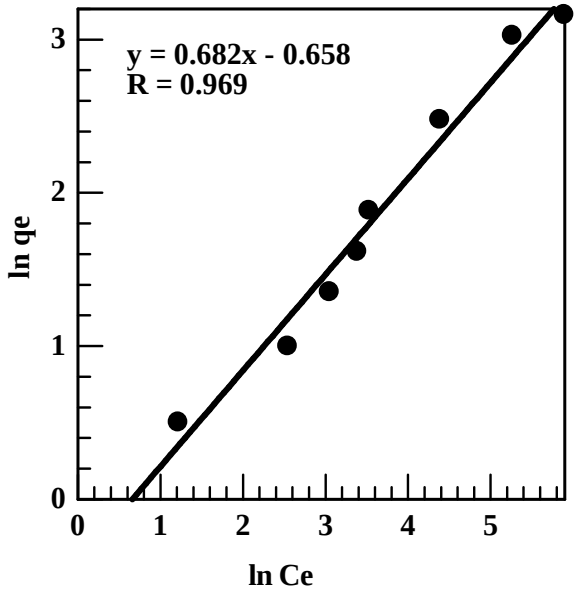

Fig.7. Freundlich isotherm for adsorption of tartrazine on to *Annona muricata L* seeds; data retrieved from Fig.4 (10-600 mg/L)

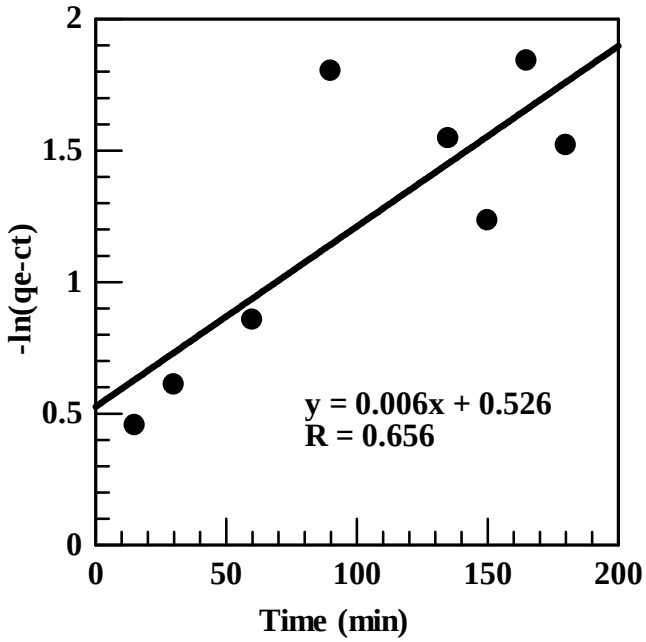

Fig. 10. Pseudo-first order kinetic model for tartrazine

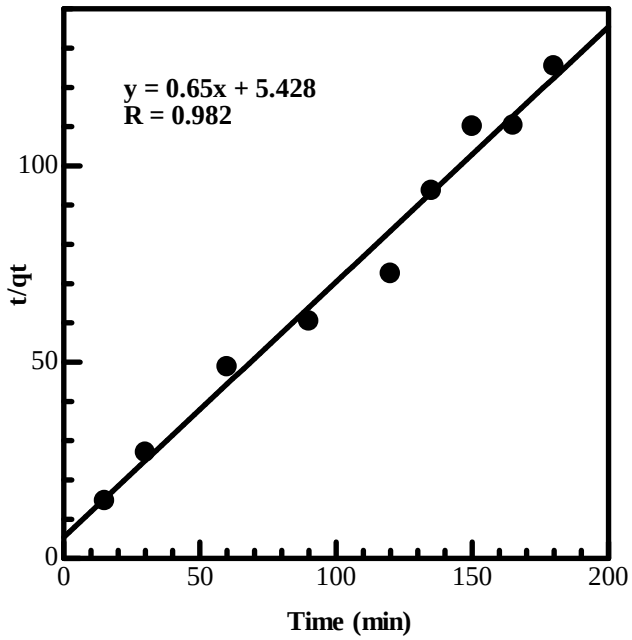

Fig. 11. Pseudo-second order kinetic model for tartrazine

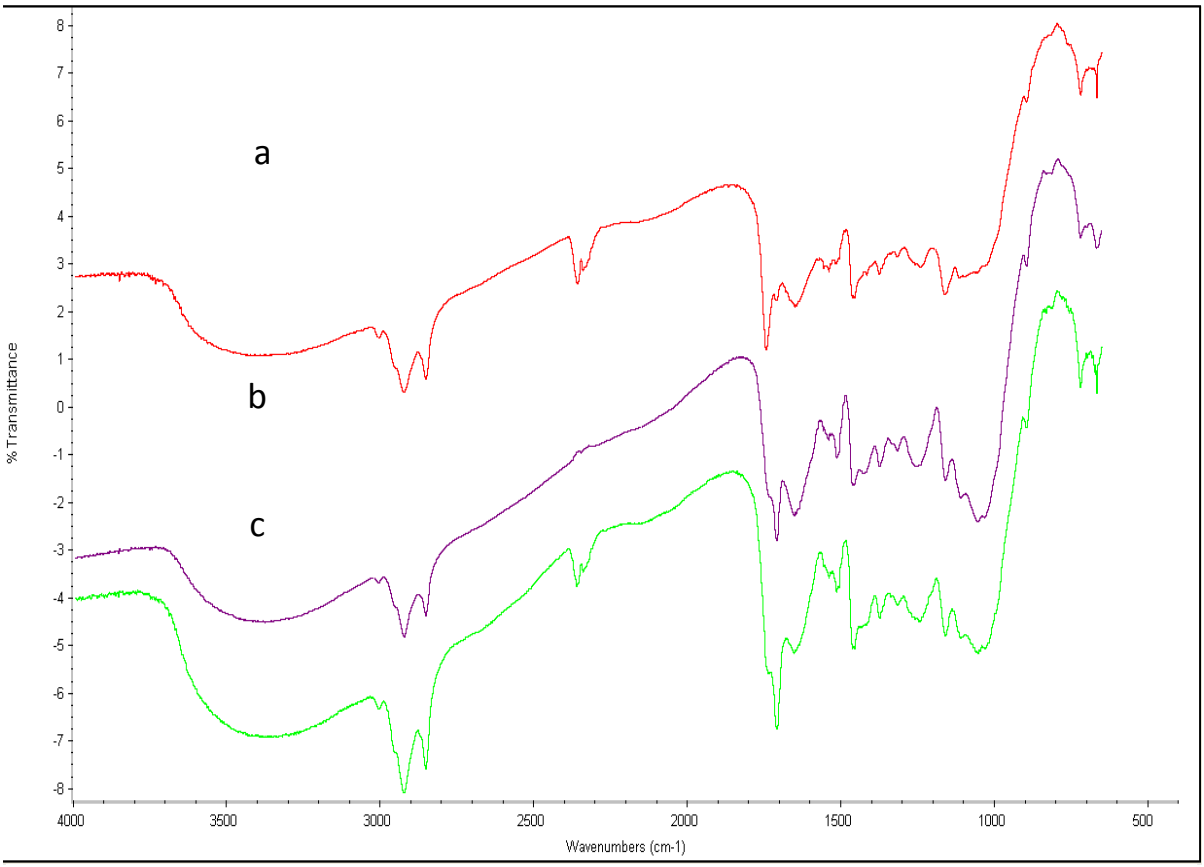

Fig.9. FTIR spectrum of *Annona muricata L* seed powder*;* (a) Before being treated (b) After being treated with HCl 0.01 M and (c) After loaded with tartrazine

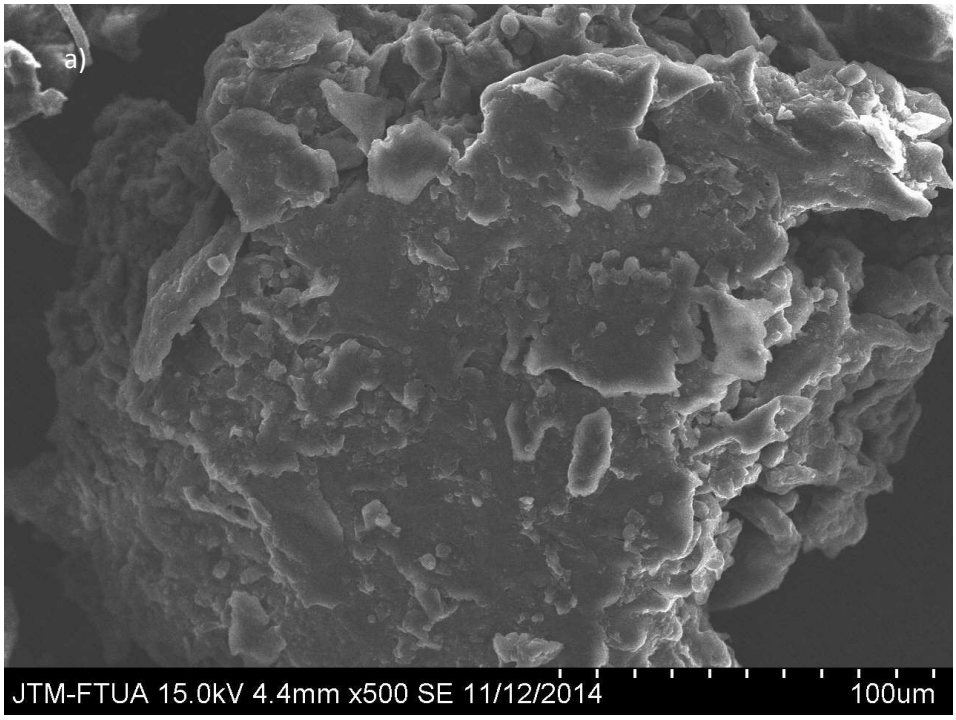

Fig. 12. SEM's Image of *Annona muricata L* seeds (a) before dye uptake. Magnifications: 500 times

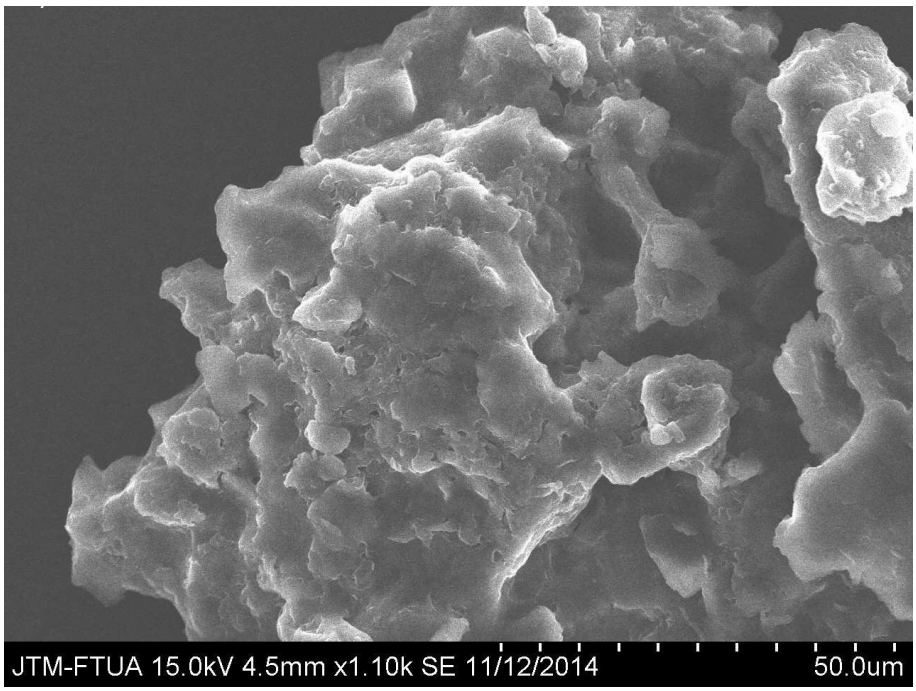

Fig. 12. SEM's Image of *Annona muricata L* seeds (b) after dye uptake. Magnifications: 1000 times

Effect of adsorbent doses on adsorption of tartrazine

Fig.5 shown adsorption capacity of tartrazine to *Annona muricata L* seeds as a function of biosorbent doses. Absorption capacity (q) decreases with increasing mass of biosorbent because of equation 1, shows the mass is inversely proportional to the absorption capacity of tartrazine. The increase in sorbent dose at constant dye concentration and volume will lead to unsaturation of sorption sites through the sorption process and secondly may be due to particulate interaction such as aggregation resulting from high sorbent dose. Such aggregation would lead to a decrease in total surface area of the sorbent and an increase in diffusional path length [20]. Adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing the adsorbent dose [19].

Adsorption isotherm

Adsorption isotherm shows the relationship adsorbate amount absorbed by the rest of the adsorbent and the adsorbate concentration in the solution. Tartrazine adsorption is other with *Annona muricata L* seeds shown in Fig.6 and 7. In this study, the value of the regression coefficient (R^2) of Freundlich's model is more suitable for tartrazine adsorption than Langmuir's model (Fig.6 and 7). Alok Mittal *et al* who studied the kinetic biosorption and tartrazine with hen feather obtain Freundlich's model is more suitable than Langmuir's model[1]. Mohammed A. Kassem *et al* showed that the Freundlich's model is better than Langmuir's model for tartrazine absorption with activated charcoal in controlled conditions [19].Based on the data obtained for adsorption of tartazine (q_m) by seeds of *Annona muricata* Lis32.2580mg/g.

FTIR analysis

FTIR characterization drawn from the analysis of the main functional groups useful in the absorption of tartrazin.The broad and intense peak at 3401.37 cm^{-1} (from the range of 3200-3600 cm^{-1}, Fig.9a),was assigned to be OH group stretching due to hydrogen bonding inter-molecular and intra-molecular polymer by compounds such as alcohols, phenols and caboxylic acid. Peak at 1745.80 cm^{-1} is the spectrum of the C=O stretching in esters (1750-1735 cm^{-1}). Peak at 1652.44 cm^{-1} showed the presence of C = O group in amide (1680-1630 cm-1). Mean while the peak of 1242.06 cm^{-1} is the CO stretching of alcohol group. Thus *Annona muricata L* seeds showed an abundance of carboxyl and hydroxyl group that may coordinate with adsorbate ions[9]. Fig.9b and 9c showed wavenumber shifted of OH group stretching 3401.37 cm^{-1} to 3378.22 $cm^{-1}$and 3374.75 cm^{-1}. In the spectrum of the C=O stretching of ester no significant changes, but the group C=O amide wavenumber shifted from 1652.44 cm^{-1} to 1654.63 cm^{-1} and 1516.16 cm^{-1}. In the OH group stretching wavenumbers shifted of 1242.06 cm^{-1} to 1259.24 cm^{-1} and 1248.00 cm^{-1}. This shifting showed that the dominant functional groups involved in absorption of tartrazine are carboxyl and hydroxyl.

Adsorption Kinetics

The kinetics adsorption data were processed to study the dynamics of adsorption process in expression of the order of rate constant. Kinetic data were analyzed with pseudo first order and pseudo second order kinetics models[21]. Equation for pseudo-first order model is

$$-\ln (q_e - q_t) = K_1.t - \ln q_e$$

Where q_e is adsorption capacity at equilibrium (mg/g), q_t is the amount of adsorbate adsorbed at time t (mg/g) dan K_1 is the pseudo-first order rate constant (min^{-1}). Equation for pseudo-second order model is

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

Where K_2 is pseudo-second order rate constant (g mg^{-1} min^{-1}).

Fig. 10. showed a linear relationship of pseudo-first order with regression coefficient, R^2 = 0.656 and K_1 = 0.006 min^{-1}. In Fig. 11. Showed a linear relationship of pseudo-second order with regression coefficient, R^2 = 0.982 and K_2 = 0.077 g $mg^{-1}min^{-1}$. Thus the kinetics of tartrazine adsorption on the *Annona muricata L* seeds fit to pseudo-second order due to high correlation coefficient. Similar report were given in various studies [9-13].

Scanning Electron Microscopy analysis

Fig. 12 shows the SEM micrograph of *Annona muricata L* seeds. It is clear from this SEM's image that the surface of material has valley, rough and porous that provides possibility for the dye to be adsorbed. Porous of material are covered by dye molecules that indicated adsorption has occurred (Fig. 12b).

CONCLUSION

The results showed that seeds of *Annona muricata L* after being treated with 0,01M HCl can be used to overcome tartrazine pollution.

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