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Research Article

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Utilization of *Annona muricata L.* seeds as potential adsorbents for the removal of rhodamine B from aqueous solution

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ABSTRACT

The ability of Annona muricata L. seeds to adsorp Rhodamine B from aqueous solution was studied using batch method. Seed was activated using HCL 0.01 mol/L . The experiment result found that the optimum condition achieved at pH 4, initial concentration of Rhodamine B 500 mg/L, biosorbent doze 0.05 g, agitation rate 100 rpm, contact time 180 second and biosorbent temperature at 70^{o}C. Biosorption capacity at optimum condition is 53.376 mg/g. The adsorption isotherms data was analyzed using the Langmuir and Freundlich. Langmuir Isotherms has higher R^2 value with 0.9009 and 0.8063 for Freundlich Isotherm. Langmuir Isotherm indicate that the process happen in adsorption was chemisorption.

Keywords: Biosorption; Rhodamine B; *Annona muricata* L. seeds

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INTRODUCTION

Wastewater from many industries such as textile, paper, rubber, plastics, paints and food containing dyes and heavy metal can cause water pollution. The huge volume of waste water containing dyes when released into the environment, cause effects on aquatic ecosystem and human life. Many dyes can cause allergic, skin irritation, dysfunction of kidney, liver, brain, reproductive, and nervous system. Rhodamine B is also carcinogenic and mutagenic and may cause irritation, redness and pain in eyes and skin. When inhaled, it cause irritation in respiratory tract. If swallowed, it can cause irritation to the gastrointestinal tract [1]. Various methods have been investigated to treatment wastewater from industry such as ion exchange, adsorption into activated carbon, membrane process, and electrolytic methods. However, the effectiveness of the most common physical-chemical processes are limited [2]. Nowadays, biosorption method has been used to remove dyes and heavy metal from wastewater using agricultural byproduct such as rice husk [3], mangosteen fruit shell [4], orange fruit peel [5], fruit waste [6], cacao shell [7] as well as other argricultural by product [8-15]. *Annona muricata* L. fruit are known for its sweetness and also sour, it well known as medicine of painful foot and back, where as their leaves has been used as hypertension medicine. *Annona muricata* L. had been used as biosorbents to remove heavy metal Pb (II) and Cu(II) from aqueous solution [16]. The aim of the present study is to examine the ability of *Annona muricata* L. seeds as a biosorbent for removal of Rhodamine B from aqueous solutions. The effects of pH of solution, adsorbent dose, dyes concentration, contact time, agitation rate and adsorbent temperature on Rhodamine B adsorption were examined. On the other hand, Langmuir and Feundlich isotherm equations were studied to quantify the adsorption equilibrium.

EXPERIMENTAL SECTION

1.1 Chemicals and apparatus

All reagents were used of analytical grade obtained from Merck. The apparatus were used pyrex, an analytical balance, a pH meter (Metrohm), crusher (Fritsch), oven (Memmert, Germany), a shaker (Haake SWB 20), mortal grinding (Fritsch, Germany), FTIR (Thermo Scientific), UV-VIS spectrophotometer (Genesys 21), and SEM (Hitachi, SU 3500, Jepang).

1.2 Treatment of soursop seeds

Annona muricata L seeds was obtained from Soursop juice producer from Padang, West Sumatera Province, Indonesia. The soursop seeds then washed with water, air dried, and ground using crusher. Then, it was dried at 60 ^{o}C in an oven for 40 h and and finally ground using mortal grinding. The working powder was activated by soaking 30 g biomass in excess of 120 mL HCl 0.01 mol/L for 2 h, followed by washing thoroughly with distillated water and then air-dried. The resulting pale brown powder can be stored for a long time as biosorbent.

1.3 Dye solution preparation

Rhodamine B was made up in stock solution of concentration 1000 mg/L and was diluted to the required concentrations (5- 700 mg/L).

1.4 FTIR Analysis

For the IR studies, 5 % (w/w) of ground and dried of soursop seeds before and after used as biosorbent were pressed to form KBr disc.

1.5 Batch biosorption studies

Adsorption experiment were carried out at various pH of the solution, contact time, agitation rate, initial concentration, biosorbent mass, and temperature under batch mode. The pH of the solution was adjusted at range 2-9 by adding NaOH, HNO_3 and buffer solution at indicated solution of pH placed in 50 mL Flask. The flask then were placed on a rotating shaker with constant shaking 100 rpm for 1 hour, and solutions were separated from biomass by using filter paper. After that, the final concentrations were determined spectrometrically at 555 nm. The metal ion uptake capacity of the biosorbent (qt, mg/g) was calculated from equation. The biosorption capacity of the biosorbent (q, mg/g) was obtained from equation.

$$Q = \frac{(Co - Ce)\,V}{m}$$

where Co and Ce were initial and equilibrium dyes concentration in solutions (mg/L), respectively; V was volume of the solution (L); m was the amount of biomass (g).

RESULTS AND DISCUSSION

FTIR analysis

The spectrum for *Annona muricata* L. seeds before adsorption (Fig.2a) demonstrates distinct peak at 3423.89 cm^{-1} representating O-H bond in alcohol, peak at 2925.24 cm^{-1} and 2854,04 cm-^{1} representing C-H streching, peak at 1745.11 cm^{-1} representing C=O in ester and 1711,83 cm^{-1} in carbocylic group, peak at 1465.44 cm^{-1} representing C-H, peak at 1244,84 cm^{-1}, 1163,63 cm^{-1} and 1117.38 cm^{-1} representing C-O in alcohol. Thus, *Annona muricata L.* seeds showed an abundance of carboxyl and hydroxyl groups. These groups present in the biomass may coordinate with rhodamine B in deprotonated forms. Several shifts of peak were observed after adsorption (Fig. 2b); peak at 2341.68 cm^{-1} and 2360,71 cm^{-1} are CO_2, impurities that comes from characterization happen. Transmittance of functional group also decrease especially hydroxyl, carbonyl and alcoholic, reveal that the main functional groups present on the surface of the biosorbents involved in the biosorption process.

SEM analysis

The SEM analysis was performed to observe the surface morphology of the biosorbents before and after dyes adsorption. The SEM image in (Fig.3a) 600 X magnification shows that *Annona muricata* L. seeds are highly porous, indicate the possibility of its good adsorption properties. After contacting with Rhodamin B, the layer of adsorbed dye are clearly visible. (Fig.3b). So, SEM analysis revealed that there were significant changes on the surface of biosorbents after interaction with dyes.

Effect of pH of solution

The pH of the solution has significant effect on adsorption process as it influences the charge on the surface of adsorbents and dyes in aqueous solution. Effect of solution pH was studied in the pH range 2 to 9, with 5 mg/L dye solution, adsorbent dose 0.1 g at room temperature and 100 rpm for 60 minutes. Figure 4 shows the optimum pH for adsorption of Rhodamine B. The adsorption capacity initially increased from 0.2462 to 0.4299 with increase in pH, with optimal uptake at pH 4. The Rhodamine B uptake, however decreased from 0.4299 to 0.3174 in the pH range 4-9. At acid condition, the Rhodamine B ion takes on a positive charge on one of the nitrogens while the carboxyl group is unionized and turn to competition with H^+ for active sites of biosorbent. When solution pH increased above 4 the carboxyl group ionized and the zwitterions form of Rhodamine B formed, that increase dimerization of Rhodamine B, which makes the molecule too large to enter the active sites of biosorbent [17].

Li Li *et al*[17] investigated the adsorption of Rhodamine B onto activated carbon derived from scrap tires and A.M el-Wakil[18] investigated the removal of Rhodamine B using dry or carbonized water hyacinth plant from aqueous solution , also got the optimal pH for adsorption of Rhodamine B as 4. On the other hand, Tabrez A.Khan [1] who studied adsorption of Rhodamine B from aqueous solution onto acid activated mango leaf found the optimum solution pH as 6.

Effect of initial concentration of Rhodamine B

The effect of initial dye concentration (5-700 mg/L) on adsorption was studied at optimized pH. Figure 5 showed the Rhodamine B biosorption capacities of *Annona muricata* L. seeds as a function of the initial concentration of Rhodamine B within the aqueous solution. The amount of Rhodamine B adsorbed per unit mass increased with an increased in initial Rhodamine B concentrations up to 500 mg/L with 46.7160 mg/g and then decreased to 33.4906 mg/g at 600 mg/L initial Rhodamine B concentration. This increased could be due to the increased in electrostatic interactions to overcome the mass transfer resistance of dye between the aqueous and solid phases and utilization of all active sites of adsorbent. At higher concentration the available adsorption sites on the adsorbent become limited, more dyes were left un-adsorbed. Tabrez A.Khan [1] investigated the biosorption of Rhodamine B onto activated mango leaf got the optimal removal of Rhodamine B at 250 mg/L. On the other hand, A.M el Waki [18] investigated the removal of Rhodamine B using dry or carbonized water hyacinth plant from aqueous solution got the optimum initial concentration of Rhodamine B at 400 mg/L.

Effect of biosorbent dose

The absorption capacity of dyes per unit mass will decrease if the adsorbent dose tended to increase. Varying the dosage of *Annona muricata* L. seeds powder within the range 0.05-0.5 g. Figure 6 showed the absorption capacity decreased with the increasing of the biosorbent dose. Tabrez A.Khan[1] investigated the biosorption of Rhodamine B onto activated mango leaf that adsorption capacity decreased with the increasing of biosorbent dose.

Effect of Agitation Rate

Effect of agitation rate was carried out by various stirring speed at 50-250 rpm showed in Figure 7 Rhodamine B has optimum values at 100 rpm with 43.5744 mg/g. The rate of adsorption is controlled by a thin layer or pore diffusion, depending on the amount of agitation [19]. The increasing of agitation rate decreases the boundary layer resistance of the transfer of adsorbate molecules from the bulk solution to the adsorbent surface and biosorption capacity will decrease if all active sites of biosorbent has benn utilized [11], whereas at low speeds the solution was suspended and it will take more time to reach the equilibrium condition.

Effect of Contact Time

The effect of contact time on biosorption capacity of Rhodamine B shown in Figure 8 was carried out by various contact time 30,60,120,180, and 240 minutes. It is clear that the biosorption capacity increase with the increase of contact time. The highest Rhodamine B uptake obtained was 51.5409 mg/g in 180 minutes and reached equilibrium in 240 minutes. P.Parimaldevi, et a [6] investigated adsorption of Rhodamine B using treated fruit waste and got the optimum contact time after 150 minutes with initial concentration of Rhodamine B was 40 mg/L.

Effect of adsorbent temperature

Figure 9 shows that with increasing adsorbent temperature from 27 to 70^{o}C, the Rhodamine B uptake increases, and decreases at adsorbent temperature 90^{o}C. This observation can be explained by the fact that the adsorbent is used organic compounds that resistant until 70^{o}C. As the high heat of adsorbent, the functional groups in adsorbent become damaged.

Desorption studies

Desorption corresponds to remove the Rhodamine B the binding site of adsorbent surface and biosorbent can be used again to removal another dye. Figure 10 show that Hydrochloric acid efficiently remove Rhodamine B from *Annona muricata* L. seeds. The greater amount of H^+, the greater amount of ion metal desorbed.

Adsorption Isotherm

The adsorption isotherm representing the relationship between the mass of adsorbate adsorbed per unit weight of adsorbent and the liquid-phase equilibrium concentration of adsorbate. In this study, the isotherm results were analyzed by Langmuir and Freundlich Isotherm. The Langmuir isotherm model assumes that the adsorption occur at homogeneous sites at adsorbent surface, and chemisorption happen, saturation happen when the dye molecule fill the site where no more adsorption can occur at that site. Langmuir isotherm can represent by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}$$

Furthermore, the favorability of adsorption was tested using a dimensionless constant called separation factor (R_L) which is an essential feature of the Langmuir isotherm:

$$R_L = \frac{1}{1 + b\ Co}$$

where Q_m was the maximum monolayer adsorption capacity of the adsorbent (mg/g), b Langmuir adsorption constant related to the free energy adsorption (L/mg), Q_e was the amount of adsorbate adsorbed at equilibrium (mg/g) and C_e was equilibrium concentration in solution (mg/L) and C_o was initial concentration (mg/L).

The Freundlich isotherm can be used for adsorption that involves heterogeneous surface energy systems . The Freundlich model equation is expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

Where K_F and n are Freundlich constants. K_F (mg/g (L/mg)$^{1/n}$) is the adsorption capacity of the sorbent and n giving an indication of how favorable the adsorption process. If the value of exponent n was greater than 1 (n >1) then the adsorption represent favorable adsorption condition[20].

Figure.1 (a) *Annona muricata* L. (b) *Annona muricata* L seeds. (c) *Annona muricata* L seeds powder

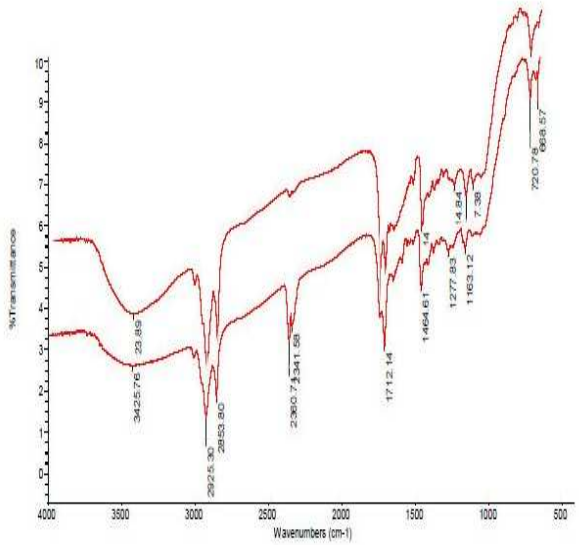


Figure.2 FTIR spectra of *Annona muricata*L. seeds (a) before and (b) after adsorption

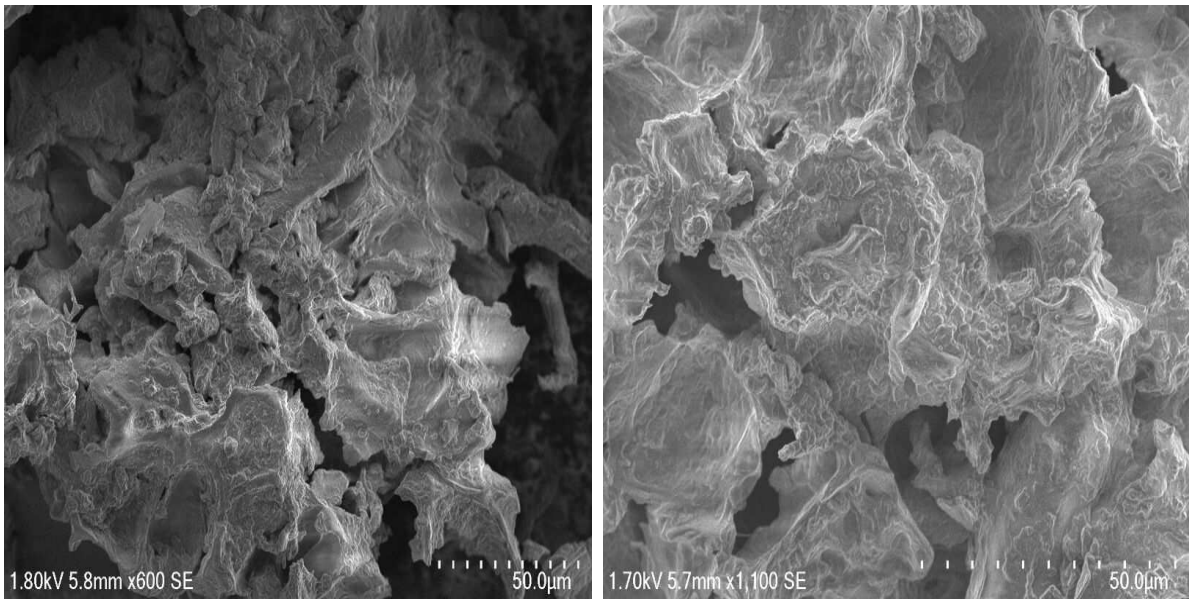


Figure.3.(a) SEM of *Annona muricata* L. seeds before adsorption 600 X 3.(b) SEM of *Annona muricata* L. seeds after adsorption 1100 X

Figure 11.a shows the Langmuir Isotherm and Figure 11.b shows the Freundlich Isoteherm.Tabel.1 lists the calculated Langmuir and Freundlich isotherm constants. From Table 1, The adsorption of Rhodamine B onto *Annona muricata* L. seeds was best described by the Langmuir isotherm model bacause of a higher value for the regression coefficient R^2 is 0,9009. The maximum adsorption capacities (Q_m) estimated from the Langmuir isotherm model is 43,4783 mg/g. Based on the RL values, the adsorption process is categorized as favorable ($0<R_L<1$) with R_L values 0.0835. It means that monolayer chemisorption of Rhodamine B occurred on the homogenously distributed active binding sites on the surface of *Annona muricata* L.seeds[14].Thus, the proposed method can be considered as a favorable uptake process for the studied dyes.

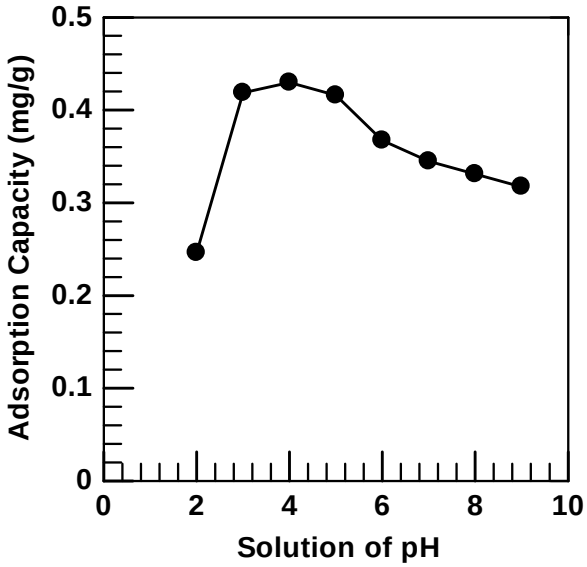


Figure.4. Effect of pH solution on the adsorption of Rhodamine B; dye solution = 10 mL; concentration of solution = 5 mg/L; biosorbent dose = 0.1 g; contact time = 60 min; agitation rate = 100 rpm at room temperature

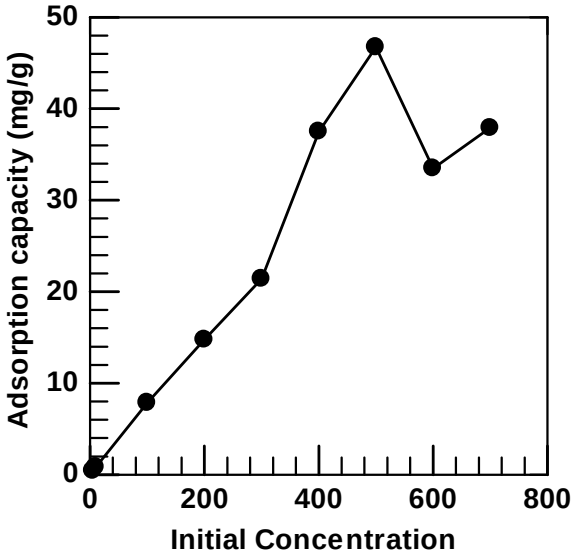


Figure.5. Effect of initial dye concentrations on the adsorption of Rhodamine B; dye solution = 10 mL; pH of solution = 4; biosorbent dose = 0.1 g; contact time = 60 min; agitation rate = 100 rpm at room temperature

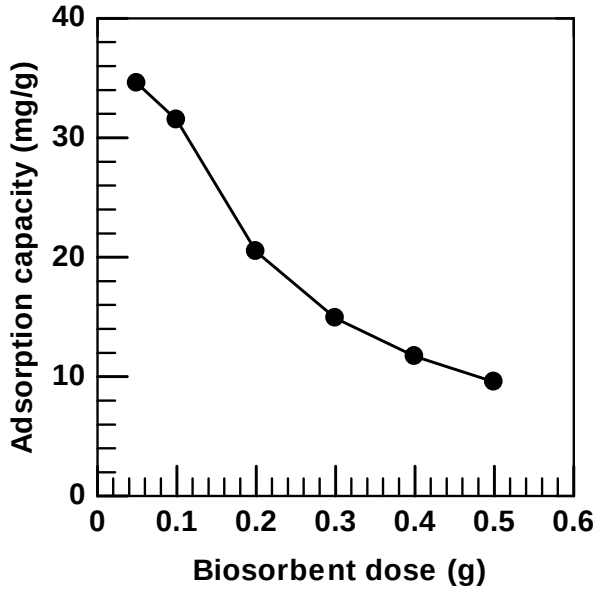


Figure.6. Effect of biosorbent doze on the adsorption of Rhodamine B; dye solution = 10 mL; pH of solution = 4; initial dye concentration = 500 mg/L ; contact time = 60 min; agitation rate = 100 rpm at room temperature

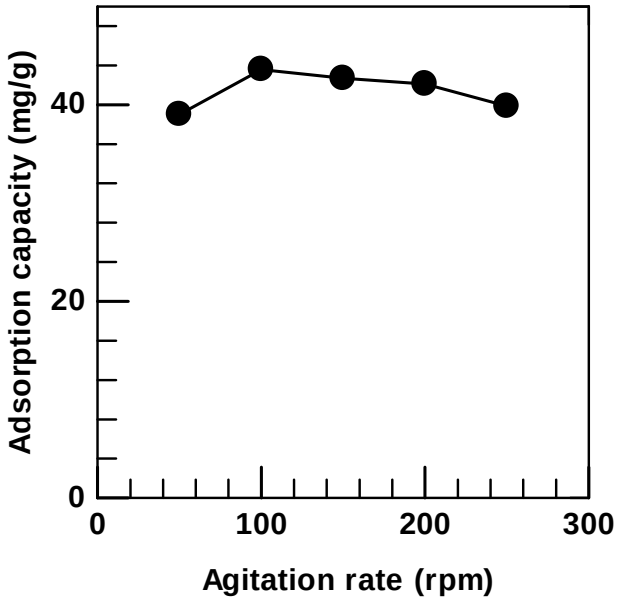


Figure.7. Effect of agitation rate on the adsorption of Rhodamine B; dye solution = 10 mL; pH of solution = 4; initial dye concentration = 500 mg/L ; biosorbent dose = 0.05 g ; contact time = 60 min at room temperature

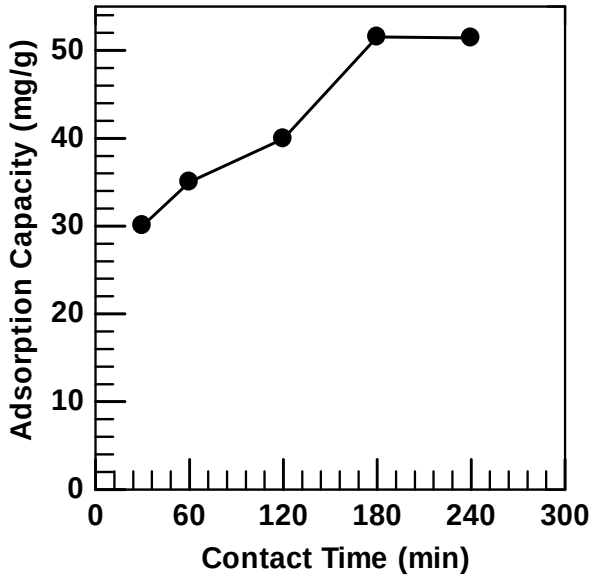


Figure.8. Effect of contact time on the adsorption of Rhodamine B; dye solution = 10 mL; pH of solution = 4; initial dye concentration = 500 mg/L ; biosorbent dose = 0.05 g ; agitation rate = 100 rpm at room temperature

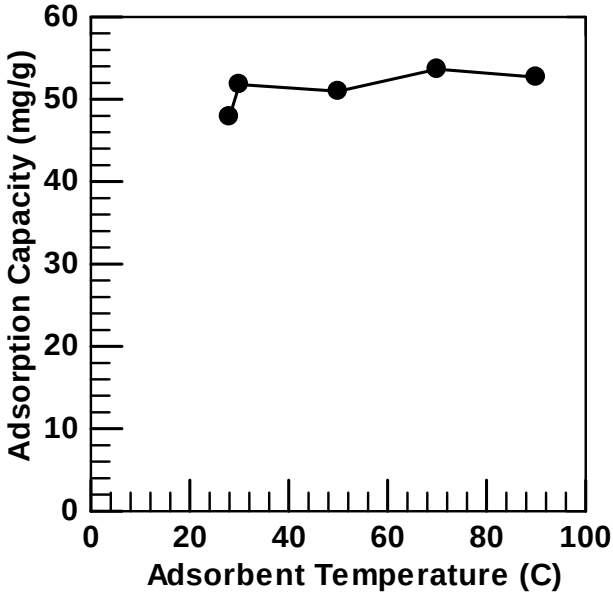


Figure.9. Effect of adsorbent temperature on the adsorption of Rhodamine B; dye solution = 10 mL; pH of solution = 4; initial dye concentration = 500 mg/L ; biosorbent dose = 0.05 g ; agitation rate = 100 rpm, contact time 180 minutes

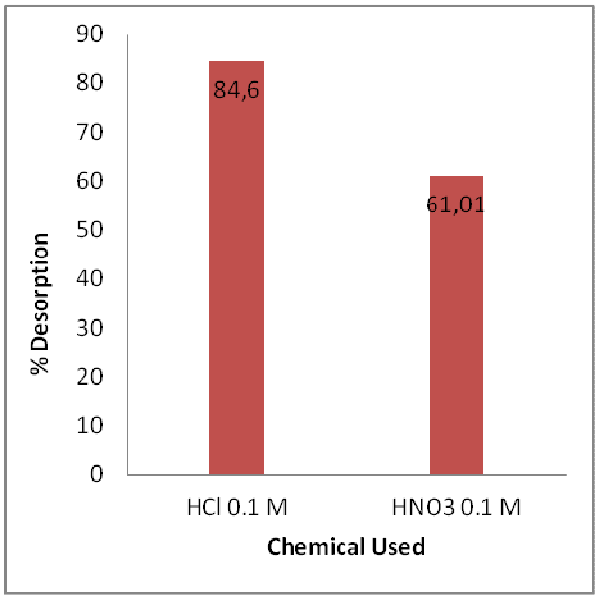
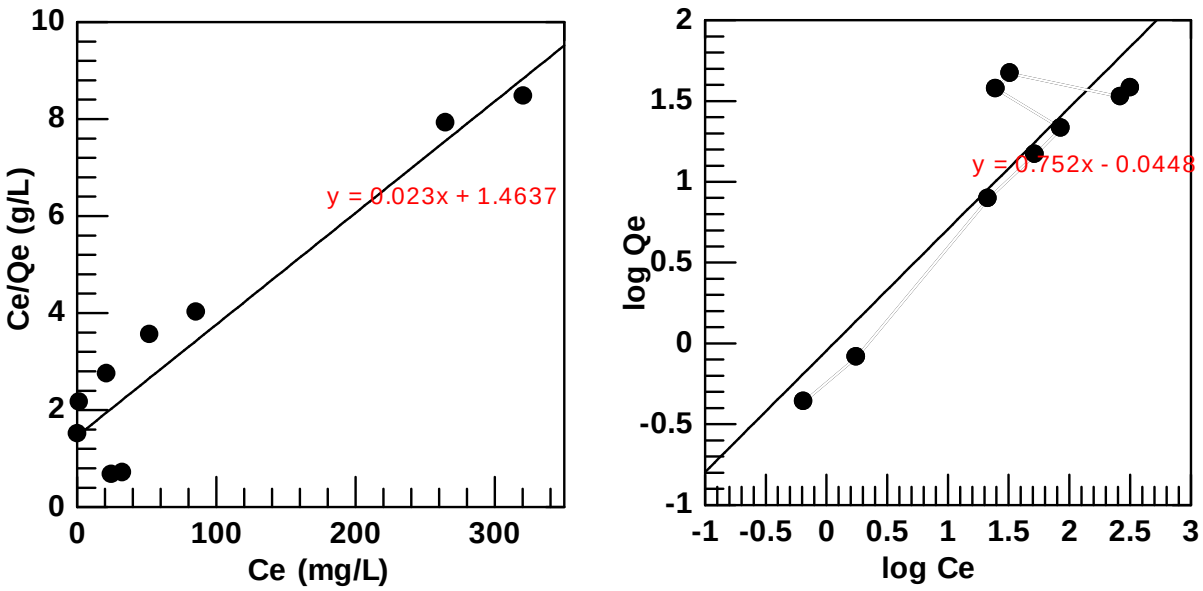


Figure 10. Graph showing % age desorption of Rhodamine B from biosorbent using HCl and HNO_3 0.1 M



(a) **(b)**

Figure 11. (a) Linearized Langmuir Isotherm (b) Linearized Freindlich Isotherm

Tabel.1 Langmuir and Freundlich parameters

Isotherm Langmuir				Isotherm Freudlich		
q_m (mg/g)	b (L/mg)	R_L	R^2	K_F	1/n	R^2
43,4783	0,0157	0.0835	0,9009	0,3565	0,752	0,8063

CONCLUSION

FTIR spectra of *Annona muricata L.* seed revealed the presence of O-H, C-H and C-O streching in the adsorbent. These groups were responsible in the process of Rhodamine B uptake since there was some shift of those peaks.

Biosorption of Rhodamin B using *Annona muricata* L. seeds showed that optimum condition of biosoprtion occurred at pH 4, initial concentration of Rhodamine B 500 mg/L, biosorbent dose 0.05 g, agitation rate 100 rpm, contact time 180 minutes and biosorbent temperature 70^{o}C, activated by HCl 0.01 M give the maximum biosorption capacity 53,376 mg/g. Fitting of Langmuir Isotherm data showed that the biosorption of Rhodamine B tended to chemisorption on monolayer adsorption with R^2 value 0,9009. This study revealed that *Annona muricata L.* seeds can be considered as an alternative biomass for removal of Rhodamine B from aqueous solution, respectively since it has high stability, relatively high in biosorption capacity, low cost, and can regenerated.

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