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BATCH ADSORPTION STUDIES ON THE REMOVAL OF AMARANTH RED DYE FROM AQUEOUS SOLUTION USING ACTIVATED *TRAPA NATANS* PEELS

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ABSTRACT

One of the escalating necessities of the current period is the removal of harmful industrial effluents. Amaranth red is extensively used anionic azo dye. Amaranth red is employed for wood, resins, textile, paper, and leather colorization. It is also used in sauces, jellies, ketchup and cake decoration as a food additive. In the present study locally available *Trapa natans* peels powder, in the form of activated carbon was used as an adsorbent. SEM results revealed a highly porous structure detected in activated *Trapa natans* peel powder ATNPP sample. The physiochemical analysis of (ATNPP) sample was performed through XRD and FTIR. BET analysis was performed to detect the surface area was 34.13 m^2/g. Various process parameters like consequence of pH, adsorbent dose, contact time, initial dye concentration and temperature were optimized during the research work. The percentage removal of amaranth red dye using ATNPP adsorbent was 86.29 %. Adsorption isotherm data was top fitted to Temkin isotherm and pseudo first order kinetics were followed. The results obtained indicates that ATNPP can be a novel adsorbent for amaranth red dye removal.

KEY WORDS : Amaranth red, Activated *Trapa natans* peel powder (ATNPP), Adsorption, Isotherms.

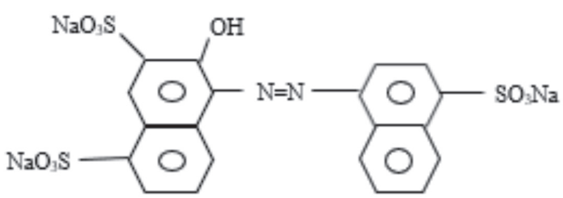
INTRODUCTION

Removing toxic contaminants from industrial wastewater would deplete their effect on environment and health (Masindi and Muedi, 2018). Wastewater generated by textile industry is generally treated by physio-chemical methods or, most commonly, by active biochemical sludge plants before being released into the environment (Bodalo-Santoyo *et al.,* 2003; Deng and Zhao, 2015). Textile waste in tones released daily and often are most common type of industrial contaminants (Kumar and Bansal, 2012). Different techniques have been used to eradicate organic and inorganics from wastewater includes, adsorption, chemical oxidation, coagulation and froth floatation etc. (Mittal *et al.,* 2005). Among these technologies, the process of adsorption has gained considerable exposure in past few years and has emerged as an successful treatment methodology (Gupta *et al.*, 2012). Azo dyes are primarily used in textile and food industries because of their specific characteristics including brilliant colors, relatively lower cost and easy processing,(around 65 – 75 percent of dyes are used globally) (Fajardo *et al.*, 2016). Amaranth ($C_{20}H_{11}N_2O_{10}S_3Na_3$) has been a well-known azo dye, commonly used for staining of textile materials, paper, wood, leather, paint and pulp (Zafar *et al.*, 2019). Moreover, For a long period, it was also used for colorization of food items such as jams, candies, ketchup and cake decoration, but in the last few years, the teratogenic and other adverse health effects of the dye have forced the authorities to ban it in many countries (Salazar *et al.*, 2013). A prolonged consumption of Amaranth may consequence in allergies, respiratory problems, tumors, and birth defects (Bernardin *et al.*, 1994; Koutsogeorgopoulou *et al.*, 1998). Activated carbon could be produced by a range of chemical and physical activation techniques and in certain cases by a combination of both types of technique (Salazar *et al.*, 2013). The properties of the activated carbon primarily based on the source materials. Activated carbon prepared from low cost waste materials by both physical and chemical activation show maximum dye removal from water and wastewater (Singh *et al.*, 2018). Experimental results of removal of amaranth dye by adsorption technique utilizing activated carbon derived from *Trapa natans* peels powder (ATNPP) as an adsorbent are reported in this research.

EXPERIMENTAL

Materials and Methods

Trapa natans locally called singhara in India was collected locally. Chemicals used for research were analytical grade which comprises Amaranth red dye ($C_{20}H_{11}N_2O_{10}S_3Na_3$), Conc. H_2SO_4, HCl and (NaOH) were procured from Sigma Aldrich Pvt. Ltd.



Amaranth

Adsorbent development

Trapa natans peels were washed with double distilled water to eradicate dirt then sun-dried for 4-5 days. This sun-dried material was further placed in oven (hot air) for 5-6 hours. Domestic mixer was used to get powder from the dried peels. Practice sized 0.125 µm (125 mesh no.) was preferred using sieve analysis. Further this powder was treated with conc. sulfuric acid H_2SO_4 in ratio 1:1 (weight/vol) (Singh *et al.*, 2020) at room temp. for one hour. Later transferred to a muffle furnace at 170 °C for half an hour to remove volatile impurities. The process of slow pyrolysis leads to a 15% yield of driven biomass which converted it into activated carbon form and then eroded with double distilled water till the pH of ATNPP became 7 and got free from acid residue.

Adsorption Studies

Adsorption studies with Activated *Trapa natans* peel powder (ATNPP) as an adsorbent was carried out by batch technique. 2 g of Amaranth red dye ($C_{20}H_{11}N_2O_{10}S_3Na_3$) was dissolved in one liter of double distilled water to get a Amaranth dye stock-solution then diluted further to get solution volumes of desired concentrations (10-100 mg/L). pH adjustment of solution was performed using HCL (0.1M) and NaOH (0.1 M). 50 ml of Amaranth solution (in 250 ml glass reagent bottle) was used for all the batch experiments. Desired pH value, contact time, adsorbent dosage and reaction temperature were optimized during batch experiments. An agitation rate of 200 rpm was given using magnetic stirrer to attain equilibration. TheAmaranth dye concentration in the solution after equilibrium were detected by using UV spectrophotometer calculating the absorbance at wavelength 520 nm. The wavelength was recorded before and after the adsorption and no peak shift was observed. The percent removal of Amaranth dye can be computed using the Equation 1 (Bhanjana *et al.*, 2017a):

$$\%\ Removal = \frac{\text{(Initial concentration of dye-concentration of dye after removal}}{\text{Initial Concentration of dye}} \times 100 \text{ -- Eqn. 1}$$

RESULTS AND DISCUSSION

Characterizations

The X-ray diffraction XRD (X′ Pert PRO) analysis were performed to determine the crystalline structure of ATNPP sample. Fourier transform infra-red FTIR (Niclot 6700) analysis were performed to explain the functional group existing on the ATNPP surface that could be engaged in amaranth removal (Kumar *et al.*, 2019a). The morphology was identified using Scanning electron microscopy (Zeiss EVO 50). The pH meter (PCSTEST35) was used for the pH measurements. The UV-Vis spectrophotometer (Rigol ultra-3660) was used to calculate absorbance.

Physio-chemical characteristics of the dried and fine pulverized ATNPP sample were assessed using XRD motif Fig. 1 (Kumar *et al.*, 2019b). The wide peak in XRD spectroscopy showed a crystalline structure of ATNPP sample. Figure 2 shown the FTIR spectroscopy of ATNPP sample. The bands at 2850-3100 cm^{-1} clearly shown the presence of analiphatic -CH group range (Saka, 2012). The wide band at 3748cm[-1] corelated with -OH range vibration and peak at 1574cm[-1] corresponds to C=C range of the aromatic rings. Two peaks at 1029 and 1710 cm[-1] are associated with vibration absorption of C–O (Xie *et al.,* 2014).

Figure 3 disclosed the micro-structure of ATNPP

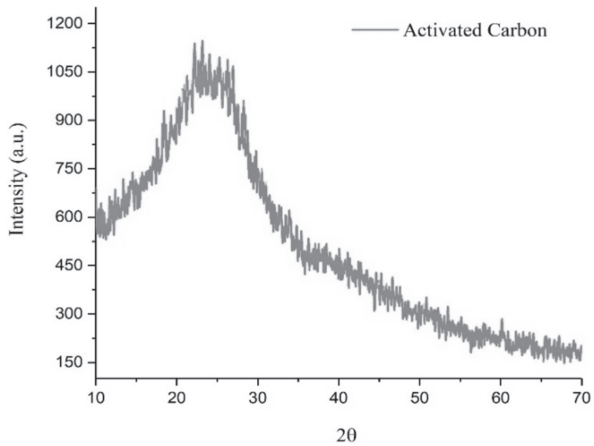


Fig. 1. XRD analysis of ATNPP sample

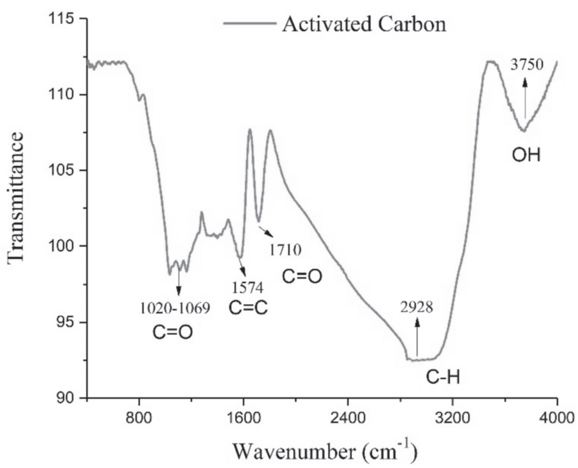


Fig. 2. FTIR spectra of ATNPP sample

sample before and after activation. In the SEM configuration, the ATNPP particles covered to be conductive are scanned in a high vacuum-chamber with a magnified range focal e[-] beam of 30-10000 resolution 200 A, 19kV of accelerated voltage. The synthesized ATNPP skeleton defines the pore configuration reported that the pore size of ATNPP sample is primarily within in the mesopore reign that provides a larger specific surface area than before activation (Xie *et al.,* 2014). This porosity of ATNPP sample has become beneficial point for amaranth dye removal.

BET Results

The most common (Brunauer, Emmett and Teller-BET) method was used to study the specific surface area of ATNPP sample (Gupta and Kumar, 2019). Based on BET measurements, 34.13 m^2/g specific surface area, 0.016 cc/g pore volume and 6.877 nm pore diameter were detected (Fig. 4).

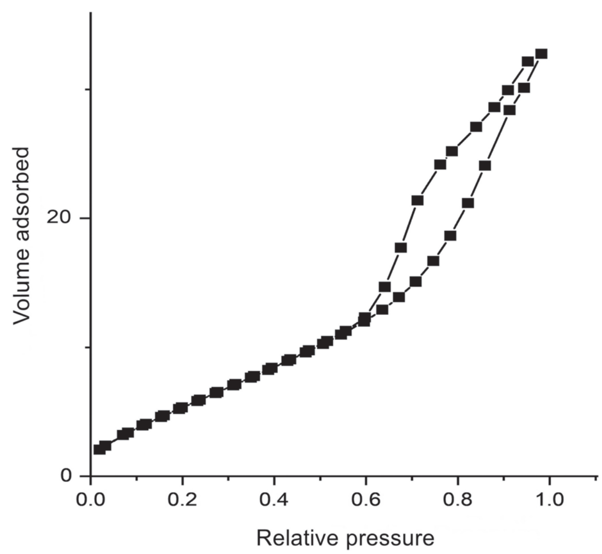


Fig. 4. BET image of ATNPP sample

Effect of pH

The adsorption activity of amaranth on adsorbent (ATNPP) was tested at room temperature with

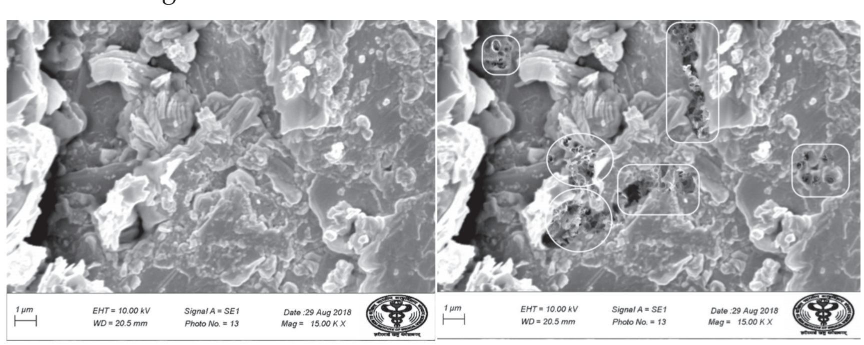


Fig. 3. SEM image of ATNPP sample

varying pH range from 2-12. In 50 ml of 50 mg/L amaranth concentration solution 0.5 g of adsorbent was added. 1N HCl and 1N NaOH respectively retained the acidic and basic solutions. Adsorption levels are also affected by H^+ and OH^- ions present in solution (Anah and Astrini, 2017). The pH has also influenced the ionization status of the adsorbent and adsorbate (Koutsogeorgoeoulou *et al.* 1998; Kumar and Bansal, 2012). It is apparent, Fig. 5 that the uptake of amaranth red decreases with rise in pH 2-12. Maximum adsorption of amaranth occurs at pH 2. This may be because the adsorbent surface was rich with H^+ charge at pH 2, thus there is a strong electrostatic force of attraction exists between the H^+charged adsorbent surface and OH^- charge of amaranth (Ndifor-Angwafor *et al.*, 2017). But, as more the pH rises, the more OH^- ions are apt to compete with anionic species of amaranth active sites. But at pH 7 there was a small rise in adsorption which may be attributed to pollutant diffusion on the adsorbent surface.

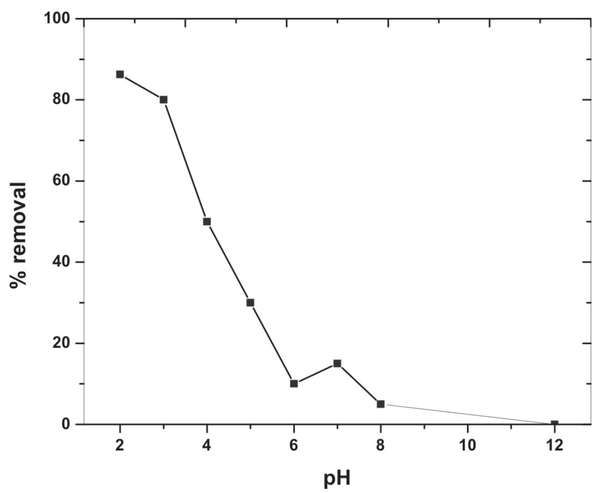


Fig. 5. Percentage removal of Amaranth dye at different pH values.

Effect of adsorbent dose

Adsorbent dose is a key factor in achieving high rate of adsorption. Several researchers have reported that the adsorption level depends on adsorbent dose (Ndifor-Angwafor *et al.*, 2017). The consequence of adsorbent dose on amaranth removal was examined at pH 2, in 50 ml of 50 mg/L amaranth concentration solution and a contact time of 120 minutes. Fig. 6 shows that since the adsorbent dose is raised from 0.1 to 1 gram, the uptake of amaranth is steadily increasing. Maximum removal at 1-gram dosage was found to be approximately 98 %. Finally, due to less contact between the adsorbent and the adsorbate present in bulk a steady value was achieved. Increased uptake of amaranth as an adsorbent dose raised could be due to the presence of more surface area and effective sites on the adsorbent surface (Gupta *et al.*, 2012).

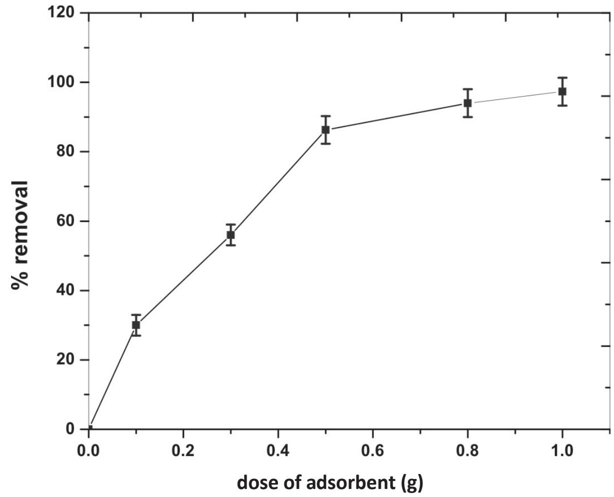


Fig. 6. Percentage removal of Amaranth dye at different adsorbent doses.

Effect of initial dye concentration

The effect of initial amaranth dye concentration on percentage removal was studied with varying dye concentrations from (20-80 mg/L) on adsorption efficiency of ATNPP at room temperature, pH 2 with a 0.5g dose of adsorbent. Fig 7 showed that there is a large decrease in percentage of dye removal at higher concentrations above 50 mg/L (Akkaya and Guzel, 2014). This may be due to the fact that at lower concentrations, all dye molecules

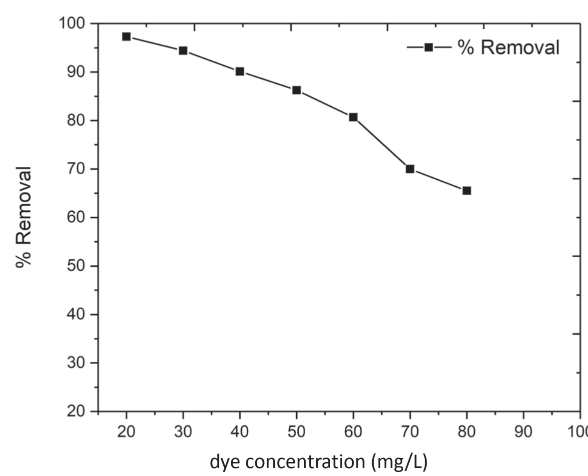


Fig. 7. Percentage removal of Amaranth dye at initial dye concentration

are bound to active sites present on the surface of adsorbent. At higher concentrations however more dye molecules remained unadsorbed due to the limited active sites present on the surface of the adsorbent due to this saturation of binding sites resulting in a reduction in the percentage of dye removal (Deniz and Karaman, 2011).

Effect of contact time

Contact time variation has a significant role in adsorption mechanism, as it enables the examination of the time needed to achieve adsorption equilibrium and study of kinetic models. Fig. 8 shows uptake of amaranth molecules with time at a room temperature, pH 2, concentration of amaranth molecules is 50 mg/L, volume of solution 50 ml and adsorbent dose is 0.5g. The result showed that the adsorption occurred in three phases. The first phase occurred very quickly during first 5 minutes because the high availability of effective sites. The second phase took around 5 to 60 minutes, when adsorption capacity was balanced. The third phase adsorption is very slow and lasted 60 to 120 minutes where the adsorption efficiency was almost constant and reflected a layer formation (Ndifor-Angwafor *et al.*, 2017).

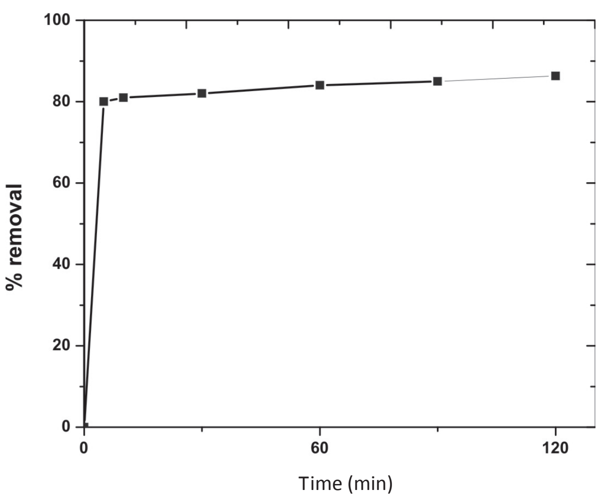


Fig. 8. Effect of contact time on percentage removal of Amaranth dye.

Effect of temperature

The temperature effect on adsorption mechanism was also examined at pH 2, concentration of amaranth dye is 50 mg/L, vol of solution 50 ml and adsorbent dosage of 0.5g at different temperatures (20, 30, 40, 50 and 60). Fig. 9 indicates changes in absorption of amaranth molecules by adsorbent (ATNPP) with a rise in temperature, thus suggesting the mechanism to be endothermic in nature (Mittl *et al.*, 2005). Increase in temperature enables the reaction to cope more efficiently with e^-/h^+recombination due to increased collision frequency of molecules resulting in increased adsorption (Gupta *et al.*, 2012).

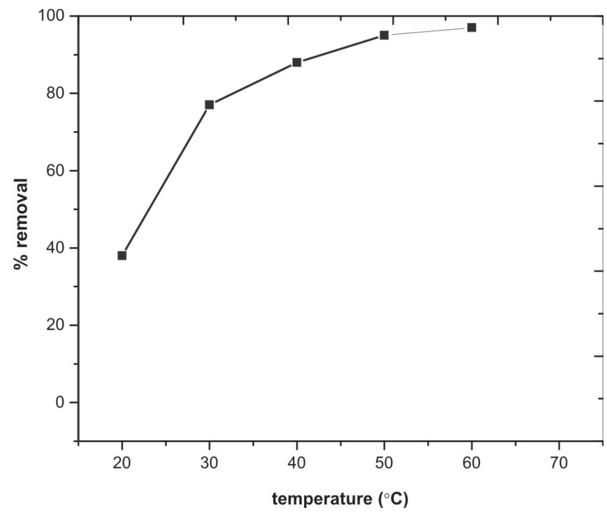


Fig. 9. Effect of temperature on percentage removal of Amaranth dye

Adsorption isotherms

D-R isotherm

The following equation was used for calculation of D-R isotherm Fig. 10 (Kumar *et al.*, 2014a; Kumar *et al.*, 2014b):

$$ln\ q = ln\ qmax - B\ e^2 \qquad \text{Eqn:2}$$

In this equation various symbols are, q = it is the constant concentration or equilibrium concentrations of Amaranth dye (mg/L) and q_{max} can be seen as maximum adsorption capacity.

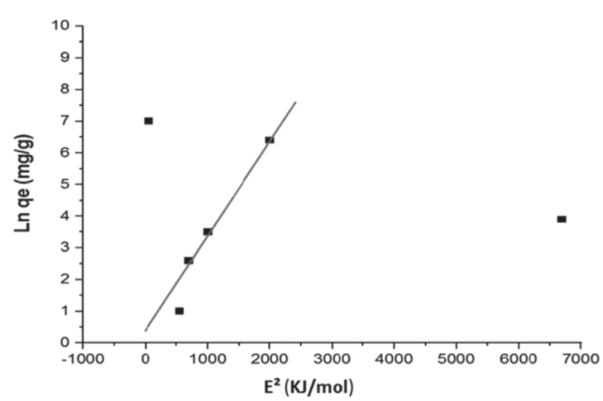


Fig. 10. D-R isotherm model for Amaranth dye removal.

Temkin isotherm

The Temkin isotherm model was found to be best suited for the present study. the equation used for model of Temkin isotherm is as follows (Bhanjana *et al.,* 2017b; Bhanjana *et al.,* 2017c):

$$q_e = RT/b \ln a C_e \qquad \text{Equation 3}$$

Where a and b are constants of temkin, R is the gas constant with T is the absolute temperature and C_e is the final concentration and q_e is the equilibrium concentration.

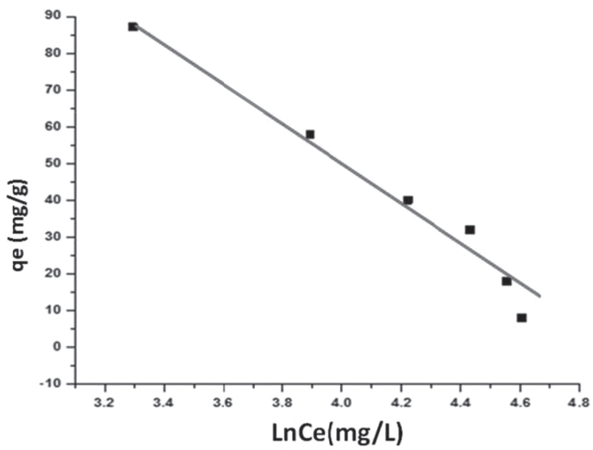


Fig. 11. Temkin isotherm model for Amaranth dye removal

Kinetic Models

Pseudo first order and pseudo second order kinetics have been used to describe the kinetic study (Kumar *et al.,* 2014a; Kumar *et al.,* 2014b) and the plots are drawn in Figure 12 and 13. The adsorption mechanism has been found to adopt pseudo first order kinetics.

Comparative study for adsorption capacity of various adsorbent materials towards adsorption of Amaranth red dye

The adsorptive capacity of ATNPP investigated in this research has been compared with other adsorbents that were reported in the literature whose values are showing in Table 1. The research outcome of the current work was compared with some other researcher work. Results of this research work revealed that the adsorbent ATNPP has higher adsorption capacity than pineapple peelings, coconut shell, peanut hull, bottom ash , de-oiled soya, alumina reinforced polystyrene (Table 1).

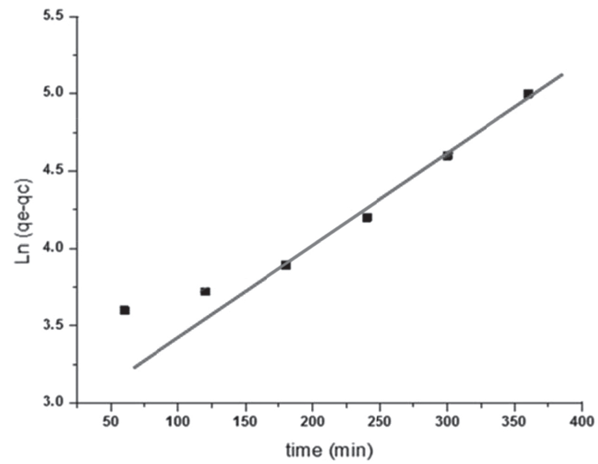


Fig. 12. Data fitting in pseudo first order kinetic model.

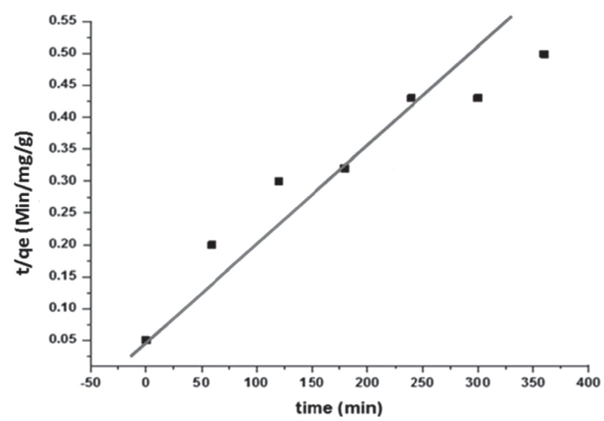


Fig. 13. Data fitting in pseudo second order kinetic model.

CONCLUSION

Bio waste material *Trapa natans* peels powder have been successfully processed and used in activated carbon form (ATNPP) as a possible adsorbent for the removal of amaranth red dye from aqueous. Kinetic mechanism has shown that uptake of amaranth dye on ATNPP followed well the pseudo first order kinetics and adsorption isotherms top fitted to Temkin isotherm model. The various batch experiments showed the maximum percentage removal of amaranth dye was 86.29 % at pH 2, in 50 ml of 50 mg/L amaranth concentration solution with an adsorbent dose of 0.5g and contact time of 120 minutes. The temperature experiment revealed that the reaction was endothermic in nature and that the adsorption rate increased as temperature increased. The findings have clearly shown that ATNPP can serve as an excellent absorber and also as cost effective than commercially available

Table 1. Adsorbent capacity values for different bio-waste adsorbents for the management of Amaranth red dye.

Adsorbents	Adsorbent capacity (mg g^{-1})	References
Pineapple pellings	31.250	Ndifor-Angwafor et al. 2017
Coconut shell	23.809	Ndifor-Angwafor et al. 2017
Peanut hull	14.900	Gong et al. 2005
Alumia reinforced polystyrene	8.281	Ahmad and Kumar, 2011
Bottom ash	7.86	Mittal et al. 2005
De- oiled Soya	12.88	Mittal et al. 2005
ATNPP	86.29	Present work

adsorbents.

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