REMOVAL OF ROSE BENGAL DYE USING SURFACE MODIFIED STRYCHNOS POTATORUM BY BIOSORPTION IN BATCH PROCESS

[1]KADAMBANATHAN, [2]KARTHIKA DURAISAMY

[1,2] ASSISTANT PROFESSOR, DEPARTMENT OF CHEMICAL ENGINEERING, AGNI COLLEGE OF TECHNOLOGY, THALAMBUR, CHENNAI. Chennai, Tamil Nadu

ABSTRACT

Textile industry produced water is a complex mixture contains Dyes, organic substances, inorganic matter and other compounds dissolved in water that ranges from fresh to brine. Discharging produced water pollutes soil surface, underground water and creates an environment hassle. Treatment of this produced water has been a challenge due to the complexity and measurement of the waste being produced, given that this unacceptable discharge requires severe treatment before disposal.

Present study investigates the adsorption performance of novel Surface Modified Strychnos Potatorum (SMSP) on synthetic Rose bengal dye solution. SMSP has showed elevated specific surface area (2630 m2 /g) and its Specific density is 1.12 g/cm^2, "excellent adsorption capacity, hydrophobicity, dye water selectivity and recycling properties. Morphology and microstructure of the adsorbent was analyzed by means of Scanning Electron Microscopy (SEM). Powder X- Ray Diffraction (XRD) was performed for phase identification of crystalline material and Fourier Transform Infrared Spectroscopy (FTIR) has been conducted to deduce the basis of chemical composition and physical state of the sample. Batch adsorption studies were carried out and effect of pH, contact time and adsorbent dosage was recorded for both synthetic and industrial sample. RB dye adsorption, equilibrium was obtained after 60 minutes of the contact time, at a pH of 2.0 and with 0.25 g adsorbent dosage, and adsorption isotherm was described by Freundlich, Langmuir and Temkin isotherms. The microscopic kinetics and thermodynamics studies onto SMSP were investigated, to describe the rate of reaction and adsorption mechanism. Pseudo second order kinetic model was observed to be the best fit the adsorption of RB dye onto SMSP. Free energy value lies in the range of physical adsorption (-20 to 0 KJ/mol), making the adsorbent regenerable and holding the feasibility in practical applications.

Keywords: Textile produced RB dye effluent, Adsorption, Strychnos Potatorum, Isotherms, Kinetics and Thermodynamics

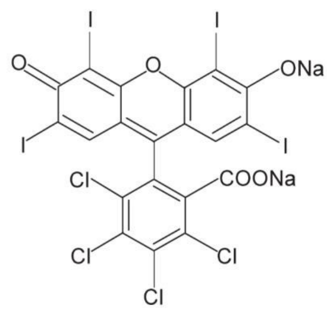
1.0 Introduction

The objective of this study is to investigate the adsorption of Rose bengal dye produced water by using the novel adsorbent SMSP and achieve 100% removal efficiency. The novel adsorbent can adsorbs Rose bengal dye of about approximately 900 times its weight. With every barrel (159 liters) of dye produced, 9 barrels (1431 liters) of RB dye produced water is released from the textile, pharmaceutical, hospitals and various sources. In the early stage, estimating properties of synthetic RB Dye produced solution, followed by characterization of the novel Surface Modified Strychnos Potatorum was studied using X-ray Diffraction (XRD) Analysis, Fourier Transform Infrared (FTIR) and Surface morphology by Scanning Electron Microscope (SEM). Batch adsorption studies are carried out with varying function of pH, contact time and adsorbent dosage. Dye adsorption of, synthetic RB dye solution is described by Freundlich, Langmuir and Temkin isotherms. “The microscopic kinetics and thermodynamics onto SMSP were investigated to describe the extent of reaction and adsorption mechanism respectively. Prior before and after to the experiment, chemical properties of Dye sample, experiment were also estimated, to conclude the variation with respect to physical properties.

Produced RB dye effluent is the largest waste stream generated in Textiles and Pharmaceuticals industries. It is a mixture of different organic and inorganic compounds, the properties vary widely depending on the residense time, clearance, and hydrochemistry of the Toxic and salts-bearing formation. On the other hand, because large volumes of produced RB dye solutions are being generated, many researchers are increasingly focusing on efforts to find efficient and cost-effective treatment methods to remove pollutants from RB dye produced effluent as a way to supplement their limited fresh water resources.

1.1 Rose Bengal dye:-

Rose Bengal(RB) is an important xanthene Anionic dye which contains Aromatic group are widely used in textile and photochemical industries, whose molecular structure as shown in Figure(1);



Figure(1):Chemical Molecular structure of RB dye

1.2 Harmfull effects of RB dye:-

Rose Bengal (RB) dye is harmful and can cause severe toxic effects on the human corneal epithelium. The dye is extremely hazardous when it comes in contact with skin and creates irritation, itching, scaling, reddening and even blistering. It also causes inflammation, redness, watering and itching in the eyes. On ingestion by inhalation it damages mucous membranes, which leads to respiratory irritation in humans.

1.3 *Strychnos potatorum Linn*:

***Strychnos potatorum Linn*.** (Fam: Loganiaceae)in locally called as Nirmali tree is grown in southern and central part of India, Sri Lanka, and Burma. It is known as Thethan tree in Tamilnadu or clearing nut tree. Sanskrit writings from India reported that the seeds were used to clarify turbid surface water over 500 years ago which indicated that they were the first reported plant-based coagulant used for water treatment.The seeds and the leaves of the tree are known for their medicinal values.The seeds contain a large quantity of an albuminous principle, upon which their virtues probably depend. Especially, its seed is used as coagulant for many centuries by the rural community. In traditional system of medicine the seeds are used for the treatment of various ailments like jaundice, bronchitis, diabetes, conjunctivitis, chronic diarrhoea, dysentery renal and vesicle calculi, leucorrhoea, gastropathy, scleritis, ulcers and other eye disease etc. The turbidity of surface water was reported to be removed by ancient people in India using *Strychnos potatorum* seeds.They are also used to clear muddy water by its coagulant action. The coagulant property was attributed to the presence of natural proteins and lipids containing functional group such as −COOH, −OH, etc., The clarification is due to the combined action of colloids and alkaloids in the seeds. They do not contain strychnine.

2.0 Method and materials

2.1 Sample collection and Preparation:-

Strychnos potatorum seeds were purchased from Siddha Shop in Mannargudi, Thiruvarur District, Tamil Nadu-India . The Seeds were washed extensively in running tap water to removing dirt like sand and other particulate matter like seed tissue and sticks. Subsequently the seeds were dried in a Hot air oven at 60°C for 5Hrs. And then the dried seeds were stored for further treatment.

Chemicals and Reagents:-

Rose Bengal dye, Potassium dichromate for Chromium(Cr) metal ions, Zinc Sulphate for Zinc(Zn) metal ions, Lead nitrate for Lead(pb) metal ions and Sulfuric acid from the chemistry laboratory of Agni college of technology-Chennai.Hot air oven for avoid moisture from the seed, Tray dryer to dry a mass , Rotary shaker which is used for the continuous shaking , Vacuum filter to separate a adsorbent from the batch solution and UV-Visible Spectrometer were used in the Institution Laboratory for know the concentration of the adsorbate.

2.3 Methodology:-

Unit operations (crushing, grinding & sieving)
Acid treatment
Mass transfer
Filtering
Analyzing

Unit operations

The unit operations were handled in the process as to crush a raw seeds into a different sizes by manual, then the crushed seeds were grinded in a Mill for size reducing to increase a surface area. Finally the sieving is taken for the separation based in the sizes.

Figure (2): Raw Strychnos Potatorum seed powder

Acid treatment

The acid treatment is a process which is used for Modify or changing the surface area of the material which is treated with acids like sulfuric acid.

Mass transfer

The mass transfer is done by a Dryers, like hot air oven and tray dryer to avoiding moisture or transfer the mass from the material to atmosphere.

Filtering

The process filtering is used for to separating the crumps or a solid particles present in a solution by using Vaccum filter.

Analyzing

The analyzing method is necessary for the report making with a proper research. The spectroscopy is the instrument that used for analyze the concentration of sample.

3.0 ADSORBENT PROPERTIES AND ITS CHARACTERIZATION

.
3.1 Adsorbent Properties;-

SMSP is eco-friendly, inflammable, degradable, non-toxic compound derived from natural *strychnos potatorum* in the form of powder. The specific density of RSP is about 0.91g/cm^2 and a Theoretical specific density of SMSP is about 1.12g/cm^2 was determined by in the lab-scale measurement and the SMSP is a hydrophobic in nature, has high adsorption capacity. Also the SMSP is so much vary from the normal activated charcoal.

3.2 Characterization of Adsorbent:-

Morphology and microstructure were analysed by means of Scanning Electron Microscopy (SEM). Powder X-Ray Diffraction (XRD) was performed for phase identification of crystalline material. The characterization results (raw data) of XRD are recorded in the supplement material.

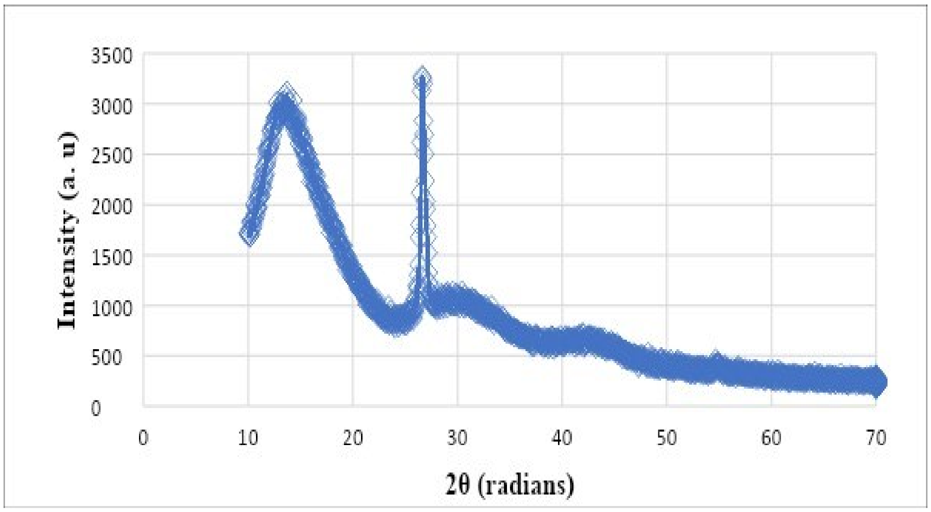
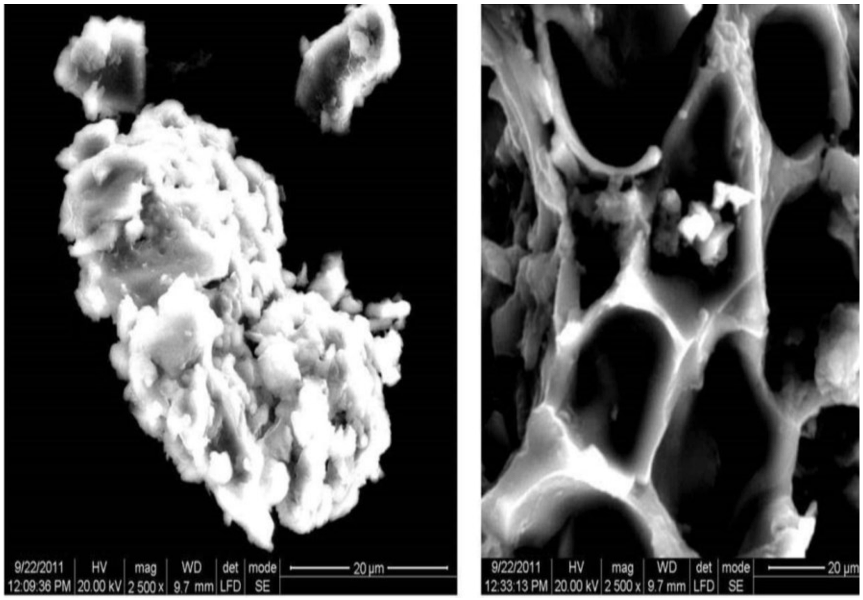


Figure (3) XRD Analysis of Adsorbent

From figure 3 (XRD), the characteristic peak for SMSP was achieved at 26.62 radians.

The pore size was calculated by Debye-Scherrer formula, D= 0.9 ()β COS θ and it was found to be 11.96 nm. Here, D is Size of a crystal, λ is the wavelength of X-ray, θ is the Braggs angle in radians and β is the full width at half maximum of the peak in radians.

Figures 2 (a) and 2 (b) show the SEM images of RSP and SMSP, respectively. From Figure 2 (b), it is clearly observed that SMSP has a considerable number of porous sites on its surface than RSP, which indicates that SMSP has better morphology for MB dye adsorption. SEM images revealed the flaky bag structure of the adsorbent revealing the presence of carbon content in it.



(Figure *4 (a)(b)* SEM Images of Adsorbent)
(From Figure 4 (a) is the SEM image of RSP and Figure 4 (b) is the image of SMSP)

The adsorption capacity of an adsorbent mainly depends on the porosity and the chemical reactivity of the functional groups on its surface. The FTIR spectrum of the RSP is shown in Figure 3 (a). The intense peak at 3399 cm^{-1} is due to −OH stretching vibration of water and stretching vibration of amine. Presence of NH2 is confirmed by N−H bending vibration at 1524 cm^{-1} and C−N stretching vibration at 1218cm^{-1}. Presence of H2O is confirmed by vibration at 1644 cm^{-1}. The peaks at 2830 cm^{-1} and 2977 cm^{-1} are due to −CH2vibration of alkyl group. The intense peak at 1050 cm^{-1} is due to −CO stretching vibration of ether groups. IR Spectra reveals that the seed mainly carries aliphatic grouping with ether linkages and amine groups.

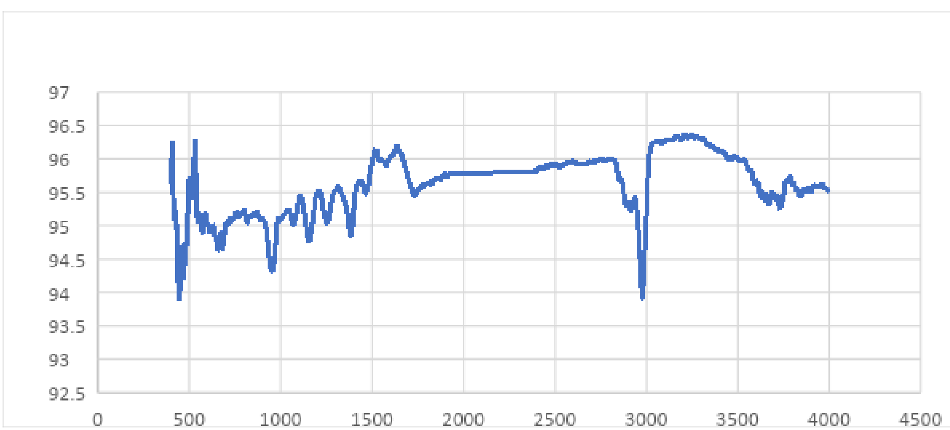


Figure (5) is the FTIR spectrum of RSP

The FTIR spectrum of the acid treated sample (SMSP) is shown in Figure 3 (b). It shows

−OH stretching vibration of H 2O at 3415 cm^{-1} and bending vibration at 1628 cm^{-1}. Presence of amino group is evidenced by the C−N stretching vibrations is close to 1304 cm^{-1}. −CH2 stretching vibration of alkyl group occurs just below 3017 cm^{-1}, but the intensity was slightly less than the RSP which is 3019 cm^{-1}. Presence of carbonyl group C═O is evident by the peak close to1731 cm^{-1}. The C−O stretching vibration of ether shows a peak at 1108 cm^{-1} and 1083 cm^{-1}. The peaks at 876 cm^{-1} and 959 cm^{-1} are assigned to cyclic ethers, since the alkyl groupings are nearly absent as their bending vibration are completely absent.

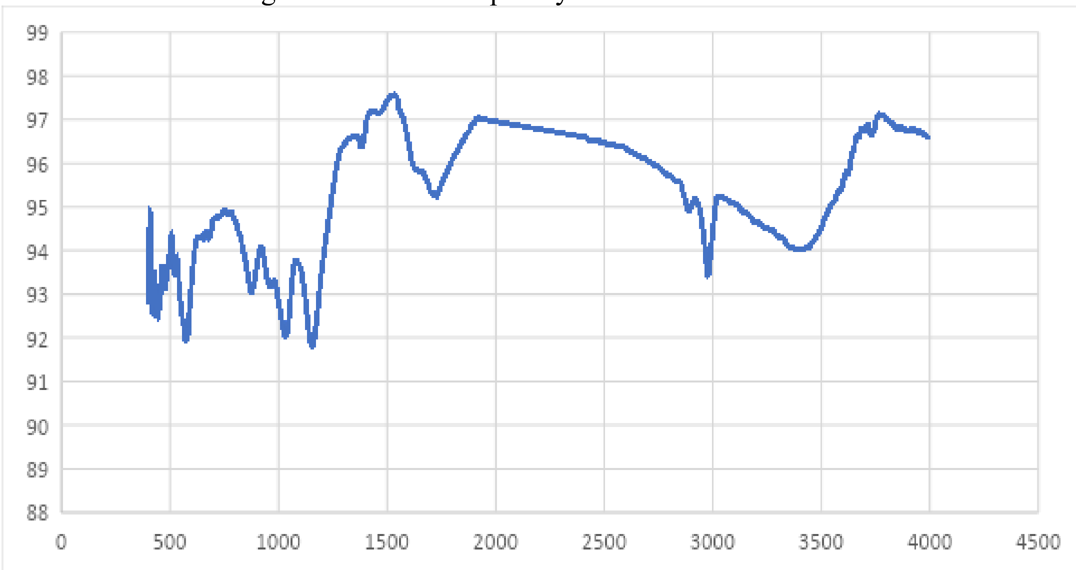


Figure (6) is the FTIR spectrum of SMSP

Methods of batch process:-

Preparation of Adsorbent:-

Collects a *Strychnospotatorum* seed and washed thoroughly in double distilled water for removing of dust particles like sand, peels etc,. Then the seed has dried in a Hot air oven at 80°C for 1 hour 30 minutes and it is crushed into a powder forms which is called *Raw strychnospotatorum* (RSP). Figure

Figure (7) Sulfuric acid treatment

Then take a 50 grams of RSP, add a 4-5 ml of sulfuric acid on it and it exhibits a exothermic reaction(Heat). Hence it turns into black colour with smoke. Then the mixture of acid and RSP was kept for 24hours in a closed surroundings to avoid contaminant and the mixture is turns into a slurry consistency.

After that, the slurry is dried in a Bunsen burner at 50°C for 3-4 minutes to remove excess acid. And collects a adsorbent (SMSP) in a air tight pack which is used for adsorption and characterization of adsorbent.

Figure (8) : Surface Modified Strychnos Potatorum

Preparation of Synthetic Dye:- Take a synthetic Rose Bengal Dye which is used in a chemistry laboratory. And take a five 1000 ml capacity Conical flaskand filled with 1000 ml of double distilled water. Then make a synthetic dye solution by adding a dye onto the conical flask in the range of 50mg/l, 100mg/l, 150mg/l, 200mg/l, 250mg/l respectively.And the conical flasks are kept in a dark surrounded place for avoiding the photodegradation. Then each of the samples dye solutions are tested for pH range and UV-spectroscopy for determining the wavelength of each samples.

Figure (9) Rose Bengal dye solution makeup

BATCH ADSORPTION EXPERIMENTS:-

A series of batch adsorption experiments were carried out to study the adsorption kinetics, adsorption mechanism, adsorption isotherm, and adsorption thermodynamics.

The batch adsorption experiments were carried out by varying parameters such as solution pH, adsorbent dose, contact time, initial RB dye concentration, and temperature to study the percentage removal of RB dye from its aqueous solution. These tests were performed to examine the effect of initial pH, adsorbent dosage, contact time on the adsorption of Rose Bengal dye on SMSP by differing the parameter under investigation and keeping alternate parameters as constant.Each investigation was done in 250 ml conical flask with 100 ml synthetic RB dye solution of known concentration and adsorbent dosage. The variation of pH (2-8) and adsorbent dosage (0.05 g to 0.5 g) in their particular range were independently contemplated each for RB dye on SMSP.

The experimental studies were conducted by taking 100 mL of RB dye solution of desired concentration in 250 mL Erlenmeyer flask. Optimum quantity of SMSP was added to each of the experimental solution and the mixture was agitated in a laboratory Rotary shaker at 160 rpm.

Figure (10) : Batch adsorption process-Filltering

The experimental contact time was varied from 10 to 80 min. At various time intervals, the flasks were withdrawn from the Rotary shaker and then the mixture was centrifuged to separate the adsorbent and supernatant. The residual dye concentration in the supernatant was measured by using UV–Vis Spectrophotometer. The percentage removal of RB dye was calculated using the following equation:

$$\% \text{ Removal of MB dye} = \frac{C_i - C_f}{C_i} * 100$$

where C_i is the Initial concentration of RB dye solution in (mg L^{-1}) C_f is the final concentration of RB dye solution in (mg^1) respectively.
The amount of RB dye adsorbed onto the SMSP was calculated by the following mass balance relationship:

$$q_t = \frac{(C_i - C_t)V}{m}$$

where C_t is the concentration of MB dye solution at time 't' in (mg/g),
V is the volume of MB dye solution in (L) and m is the mass of the adsorbent SMSP in (g).
The amount of equilibrium adsorption (mg /g), was calculated using the formula:

$$q_t = \frac{(C_i - C_e)V}{m}$$

where C_e is the concentration of RB dye solution at equilibrium (mg L^{-1}).
V is the volume of MB dye solution in (L) and m is the mass of the adsorbent SMSP in (g).
The adsorption kinetic data were tested with the pseudo-first order and pseudo-second order kinetic equations. The adsorption isotherm data or equilibrium data for RB dye removal using SMSP was tested with three adsorption isotherm models such as Langmuir, Freundlich, and Temkin. The adsorption thermodynamic studies were performed in the time interval of 303–333 K. A 0.25 g/L of SMSP with the 100 mL of various initial RB dye concentrations (50–250 mg/L) was shaken in the Thermal Rotary shaker at 160 rpm for about.

4.0 RESULTS AND DISCUSSION

4.1 Effect of pH:

pH plays an important role in adsorption mechanism, since it affects the dosage of adsorbent in an economical manner. For effect of pH, the adsorbent dosage, Contact time, Temperature are at constant for whole experiment is 0.25 g of dose for 60 minutes at 33°C. Batch experiments was carried out by adjusting pH in the range of 2.0 - 11.0, by adding HCl or NaOH, to determine the effect of pH in removing dye from synthetic dye solution. The influence of pH on adsorption behaviour of SMSP for dye removal is shown in Figure 6 (a).It can be seen that the removal efficiency and coagulation activity of SMSP on dye was highest for adsorbent at pH 2.0.

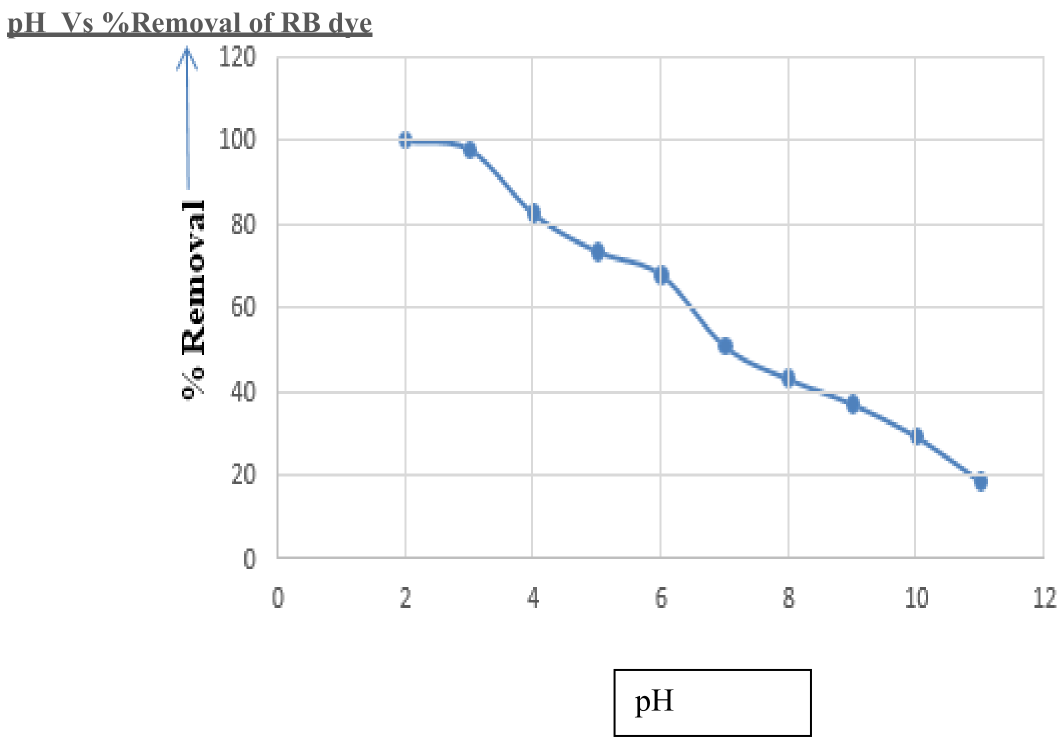


Figure (11): Effect of pH in the Rose Bengal dye on SMSP

The removal capacity of the adsorbent started decreasing after pH 2.0. Percentage removal of RB dye increases with an decrease in solution pH till the pH 2. Maximum removal of RB dye was observed at the optimum pH of 2.0. Also, when the value of pH was high the charge of the SMSP would be less positive and as a result it would become less attractive to the anionic organic compounds (anionic dye).Since almost 50% adsorption of the dye was achieved at pH 7.00, this pH was selected for all subsequent studies.

4.2 Effect of Adsorbent Quantity:-

The RB dye uptake capacity of SMSP on synthetic RB dye solution using different amounts of SMSP (0.25-0.55g) was recorded. For the effect of adsorbent dosage, the contact time, temperature and concentration of RB dye solution remains constant for whole experiment about 100 ppm for 60 minutes at 33°C, the adsorbent dosage only vary.

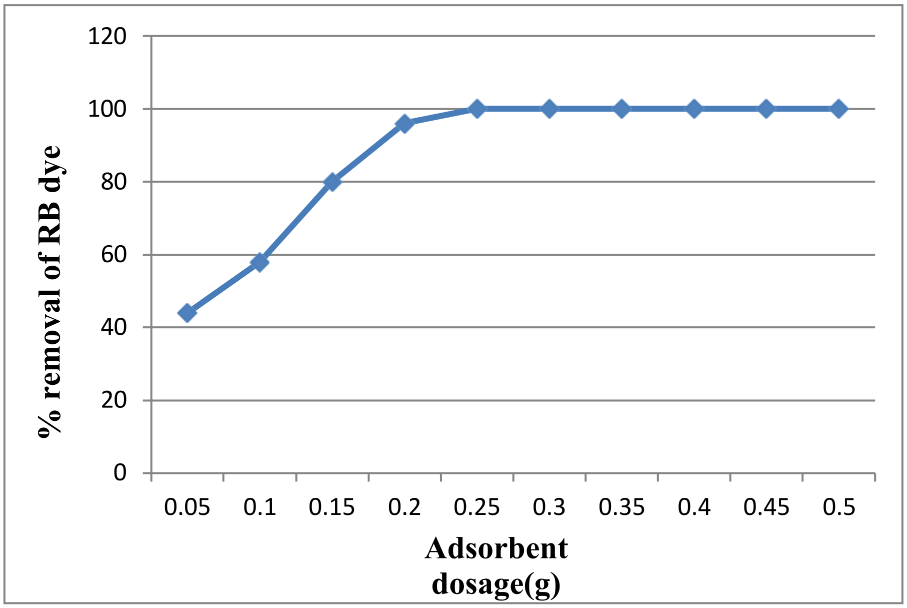


Figure (12): Effect of Adsorbent dosage in the Rose Bengal dye on SMSP

The equilibrium dye uptake capacity Qe was found to increase initially with an increase in the dosage of the adsorbent until 0.25-0.3 g and it continued to be constant after 0.25g of adsorbent dosage. And percentage of removal has widely increased with increase in adsorbent dosage. While at the intermediate stage, the adsorption rate unveils the tendency to slow down. When being around 0.25 g of adsorbent, the adsorption process reached the equilibrium. Subsequently, adsorption studies were performed by selecting 0.25 g of adsorbent.

4.3 Effect of Contact Time:-

The percentage of RB dye removal was analyzed with respect to contact time for 0.25 g of adsorbent dosage, because the Dosage optimization was studied from the effect of adsorbent dosage. The 250 ppm of RB dye solution was makeup in a Eight conical flask with dosage, pH, Temperature are remains constant for whole experiment except of adsorbing time, here the time is noted for every 10 minutes of each conical flask.

The system reached its saturation at60 minutes where 100% of RB dye was removed in the 250 ppm of synthetic RB dye solution. Temperature and pH of the system was maintained at 305 K and 2.5 respectively. And the 2.5 pH optimization was studied form the effect of pH.

Contact time Vs. % Removal of RB dye

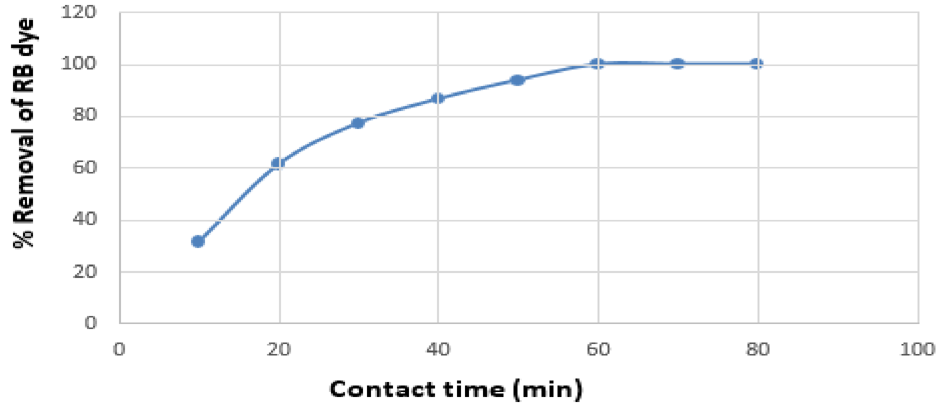


Figure (13): Effect of Contact time in the Rose Bengal dye on SMSP

4.4 Adsorption Isotherm:-

Various adsorption isotherm model was used to explain the interaction between adsorbate and adsorbent, to optimize the maximum adsorption parameters when the adsorption process reaches equilibrium. In this study to evaluate the dye adsorption capacity of novel SMSP, common isotherm models, Langmuir, Freundlich and Temkin models were adopted. Experiments are performed with best optimised parameters.

Langmuir Isotherm:-

The Langmuir isotherm model represents monolayer coverage on a homogeneous surface and there is no interaction between the adsorbed dye molecules. The Langmuir isotherm constants, Q_m and K_L were determined from the respective slope and intercept of the straight-line plot of C_e / Q_e vs C_e.

The linear form equation of Langmuir adsorption Isotherm can be demonstrated as:

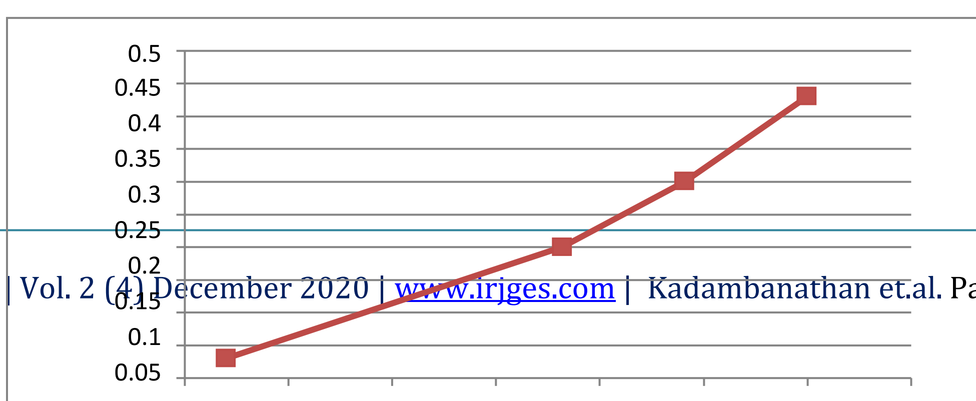
$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L}$$

In above equation,Qe is the amount of equilibrium adsorption capacity(mg g^{-1}),

Ce is the equilibrium concentration of the oil (mg L^{-1}),

Q_m represents the maximum adsorption capacity (mg g^{-1}) and

K_L represents the Langmuir constant (L mg^{-1}).



Ce/Qe (gm/L

Figure (14) Langmuir Isotherm for SMSP Adsorption

<u>Freundlich Isotherm:-</u>

The Freundlich isotherm model is generally used for heterogeneous systems and is applied for multilayer adsorption processes.

The linearized expression of Freundlich adsorption isotherm can be expressed as:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e$$

The linearized plot of log Qe Vs log Ce shows the applicability of Freundlich isotherm. The Freundlich isotherm constants, Kf (adsorption capacity) and 'n' (surface nature) can be calculated from the Freundlich linear plot.

In above, Qe is the equilibrium adsorption capacity (mg g^{-1}), Ce is the equilibrium solute concentration (mg L^{-1}).

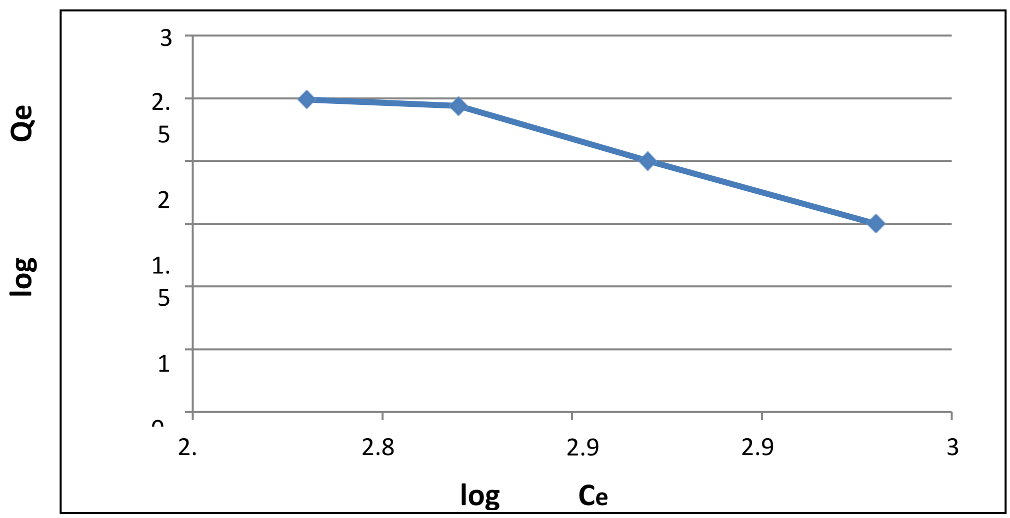


Figure (15) Freundlich Isotherm for SMSP Adsorption

<u>Temkin Isotherm:-</u>

While for the Temkin isotherm, it is assumed that adsorption heat of the adsorbate decreases linearly with the increase in surface coverage.

The linearized expression of Temkin adsorption isotherm can be expressed as;

$$Q_e = b \ln K_T + b \ln C_e \ ; \quad b = \frac{RT}{A}$$

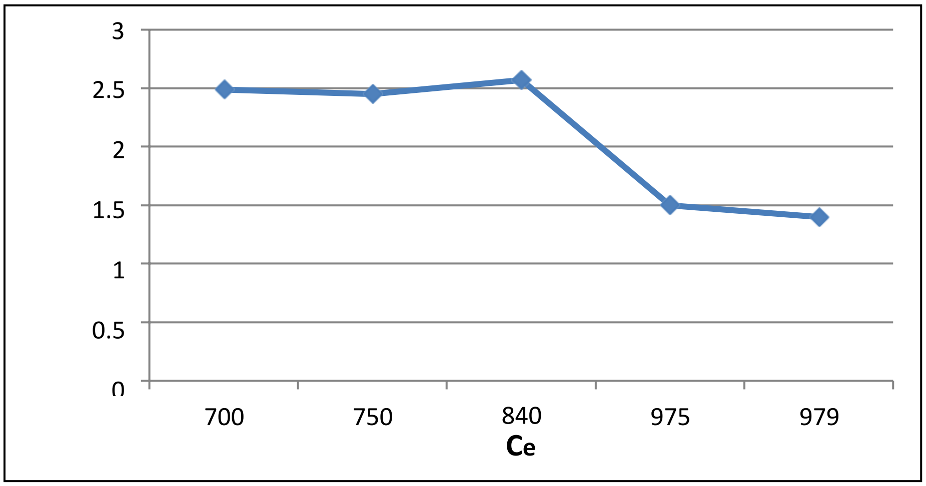


Figure (16) Temkin Isotherm for SMSP Adsorption

The above figures, describe the relationships between the dye equilibrium concentrations and adsorption capacities of SMSP, and the fitting results exhibit variance (R^2) of three models; remarkably, this parameter of Freundlich was higher than that of other models for synthetic RB dye solution (R^2 = 0.9811) samples, suggesting multilayer adsorption. Besides, the Freundlich model constant (1/n) is 0.7346, revealing that the adsorption process was favourable.

Freundlich			Langmuir			Temkin		
KF	1/n	R^2	KL	Qm	R^2	KT	b	R^2
170.86	0.7346	0.9811	0.0045	32000	0.9643	0.0054	6090	0.876

4.5 Adsorption Kinetics:-

To understand the acuteness of adsorption reaction and extent of reaction, constructing a mathematical model becomes indispensable. In this study pseudo- first order, pseudo-second order were applied. Lagergren's first order rate equation is the most known to express the adsorption rate based on adsorption capacity.

The linear form of Lagergren's first order equation:

$$\ln(Q_e - Q_t) = \ln(Q_e) - k_1 t$$

The Lagerren's Second order rate equation are as follows:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$

Where, Qe (mg g^{-1}) denotes equilibrium adsorption capacities and Qt (mg g^{-1}) adsorption capacities at time t.
k1 (min^{-1}) is the reaction rate constant of the pseudo first order kinetics. The values of k1 and Qe is obtained from the slopes and intercepts of 'ln (Qe − Qt)' versus 't' plots.

k2 (g mg^{-1} min^{-1}) is the pseudo second- order rate constant. The values of Qe and k2, is obtained from the fitting line of 't /Qt' versus 't' and the correlation coefficient (R^2) was used to evaluate the fitting results.

Adsorbent dosage (mg)	**K1 (min^{-1})**	**$(R1)^2$**	**k2 (gm mg^{-1} min^{-1})**	**R2 2**
0.05	0.2739	0.9695	0.00049	0.997
0.1	0.1906	0.9691	0.0005	0.9942
0.15	0.18	0.9538	0.0005	0.9977
0.2	0.1543	0.9454	0.00049	0.9945
0.25	0.0837	0.9438	0.0005	0.9954

Table 1 Adsorption Kinetics for Synthetic RB dye Sample(Pseudo First and second order reactions)

From the kinetic data, it was found that the experimental capacity best fits with the pseudo second order kinetic model for the adsorption of dye onto SMSP with (R^2 = 0.9977) for synthetic RB dye solution. This gives us an inference that diffusion is the mechanism that drives the process of dye adsorption. The foremost important data to verify the order is rate constant and that to be also found constant in pseudo second order kinetics. Hence, pseudo second order kinetic model is considered to be more preferable to represent the adsorption mechanism of RB dye onto SMSP.

ln (Qe- Qt)

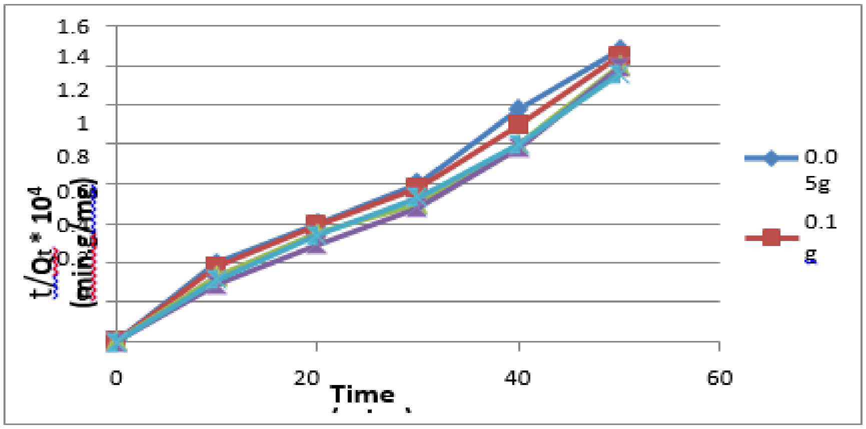


Figure 18 Pseudo Second Order Kinetic Model for RB dye

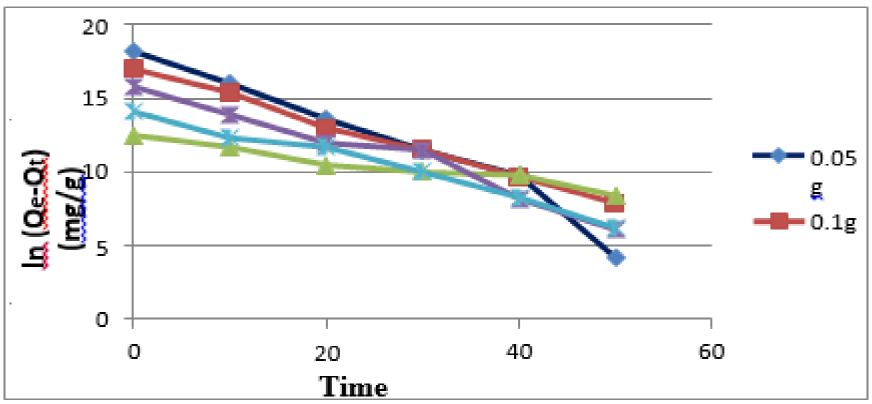


Figure 17 Pseudo First Order Kinetic Model of RB dye

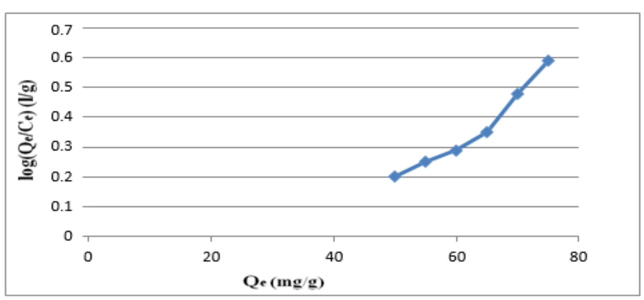


Figure 20 Thermodynamic Studies for RB dye

A reaction is consider spontaneous when it can react with another element on its own, without the help from a catalyst. ΔG^{O} is the symbol of spontaneity, and there are two factors which can affect it, enthalpy and entropy.

Enthalpy- the heat content of the system at constant pressure. Entropy- the amount of disorder in the system.
When delta G > 0 is Non-spontaneous reaction, delta G < 0 is spontaneous reaction and the delta G = 0 is at equllibrium.

The result of calculated ΔG^o is negative, −18.89 kJ mol^{-1} (for RB dye solution) thereby confirming that the adsorption behavior of RB dye onto SMSP was spontaneous and favorable in thermodynamics. Besides, if this value is between −20 and 0 kJ mol^{-1}, this adsorption can be considered as physical adsorption, and if this value is between −80 and −400 kJ mol^{-1}, this process can be regarded as chemical adsorption.

Hence here proved that the sorption is based on the Physical adsorption because of ΔG^o is belongs to the negative sign (−18.89 kJ mol^{-1} from the calculation).

Then the physical adsorption is a multilayer adsorption in which the first layers adsorbed on the adsorbent and the other layers are condense on the first layer. But the chemical adsorption is a single layered adsorption and has lower ΔS^o value than physical adsorption. Then it is proved that the adsorption is based on the multilayered adsorption.

4.6 Optimization of Dyes & Metal ions

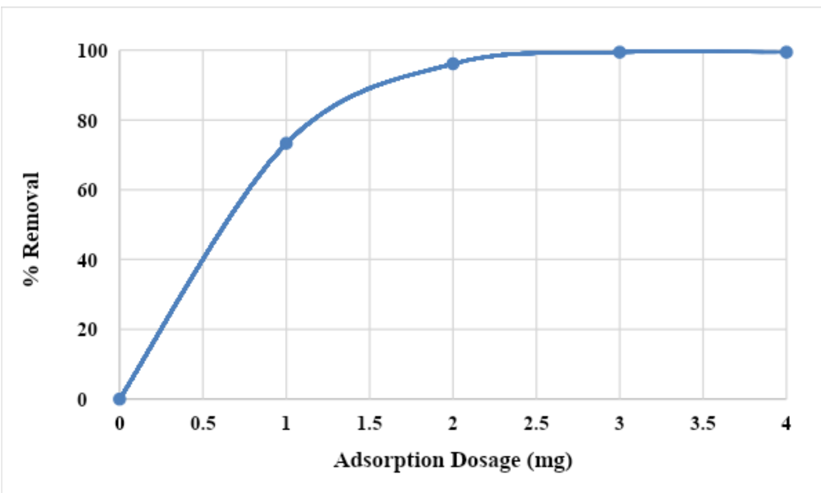


Figure 21 Process Optimization with Adsorbent Dosage

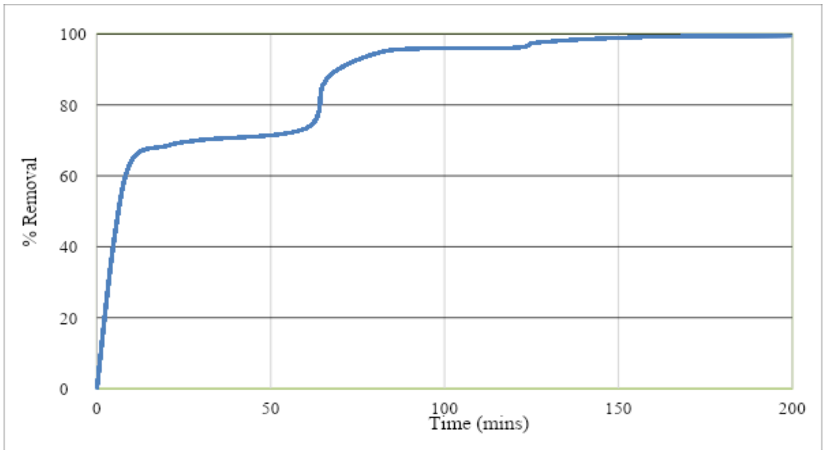


Figure 22 Optimization: Time and Dosage

0-60 mins: 0.25g of adsorbent is added;
60-120 mins: extra 0.05g of adsorbent is added (Total= 0.3g);
120-180 ns: extra 0.05g of adsorbent was added (Total= 0.35g)

5.0 Conclusion

In this study, SMSP was used as adsorbent to remove RB dye and metal ions from effluent water. Adsorption experiments were conducted in batch mode to determine the influence of operating parameters such as pH (2-8), adsorbent dosage (0.05-0.5 mg) and contact time. The optimal pH value was found at pH 2.5, adsorbent dosage of 0.15 – 0.25 g for synthetic dye. The process attained equilibrium at 60 min for dye water sample with efficiency of 100% dye removal on SMSP. For synthetic dye solution sample, maximum efficiency was found at 35 mins, with 95% dye removal. Further, the modelling of the adsorption kinetics and equilibrium data provided best fit in case of pseudo-second order kinetic model. This gives us an inference that diffusion is the mechanism that drives the process of dye adsorption Analysis of thermodynamic data revealed the exothermic and spontaneous nature of the adsorption process. The results of this study concluded the high potential of SMSP on removing Dye and metal ions from effluen water which is further affirmed by the significant characteristic features of the adsorbents as described by SEM with FTIR analysis and XRD analysis. Process optimization was opted by adding adsorbent in multiple stages with 60 mins interval and maximum dye removal is 99.46% and the metal ions 97.45% was achieved.

REFERENCE:-

1. Mohammadine El Haddad, Rachid Slimani, Rachid Mamouni, Said ElAntri, Said Lazar (2013) ‘Removal of two Textile dyes by Calcined Bones’, Journal of the Association of Arab Universities for Basic and Applied Sciences.
2. Sahar Peyghami, Soheil Sharifi, ForoughRakhshanizadeh, Khalil Alizadeh , Nonlinear optical properties of Rose Bengal: Effect of environment, Journal of Molecular Liquids(2017)
3. Mu. Naushada, Zeid Abdullah ALOthmana, Md. RabiulAwualb, Sulaiman M. Alfadulc&TansirAhamada, (2015) ‘Adsorption of rose Bengal dye from aqueous solution by amberlite Ira-938 resin’ Desalination and Water Treatment.

4. Vinod Kumar Gupta, Alok Mittal, DamodarJhare and Jyoti Mittal, (2012) 'removal of hazardous colouring agent Rose Bengal by adsorption techniques using bottom ash' RSC Advances dynamic Articles.
5. Mohamed A. Ahmed, Nader M. Abdelbar, Ashraf A. Mohamed,(2017) 'Molecular imprinted chitosan-TiO2 nanocomposite for removal of Rose Bengal dye from waste water' International Journal od Biological Macromolecules.
6. GuoqiangShen,LunPan, ZheLü,ChongqingWang, Fazal-e-Aleem, Xiangwen Zhang, Ji-Jun Zou,(2018) 'Fe-TiO2andFe2O3 quantum dots co-loaded on MCM-41for removing aqueous rose Bengal by combinedadsorption' ChineseJournalofCatalysis39(2018)920–928.
7. Sadia Ameena, Hyung-Kee Seo, M. ShaheerAkhtarb,Hyung Shik Shina, (2012) 'Novel graphene/polyaniline nano composites and its photocatalytic activity toward the degradation of rose Bengal dye' Chemical Engineering Journal 210 (2012) 220–228.
8. Aleksandar Cvetkovic, Adrie J. J. Straathof, RajamaniKrishna, and Luuk A. M. van der Wielen,(2004) 'Adsorption of Xanthene Dyes by Lysozyme Crystals' Langmuir 2005, 21, 1475- 1480 in American Chemical Society.
9. Vinuth M, Naik HSB, Vinoda BM, Pradeepa SM, Arun KG, et al. (2016) Rapid Removal of Hazardous Rose Bengal Dye Using Fe(III)– Montmorillonite as an Effective Adsorbent in Aqueous Solution. Journal of Environment Anal Toxicol 6: 355.
10. V Nandhakumar, A Rajathi, R Venkatachalam, K Ramesh and S Savithiri, (2015) 'Adsorption of Rose Bengal Dye from Aqueous Solution onto Zinc Chloride Activated Carbon, SOJ Materials Science & Engineering.
11. P. Lakshmipathiraj,S. Umamaheswari, G. Bhaskar Raju, S. Prabhakar, G. Caroling, S. Kato, and T. Kojima, (2011) 'Studies on Adsorption of Cr(VI) onto Strychnos potatorum Seed from Aqueous Solution', Environmental Progress & Sustainable Energy (Vol.00, No.00) in AIChE.
12. Sanmuga Priya E and Venkataraman S, (2010) 'Pharmacognostical And Phytochemical Studies Of StrychnosPotatorum Linn Seeds' PHCOG J.
13. M. Kirupa Sankar K. Muthu Kumar B. Ranganathan V, (2014) 'Adsorption of anionic azo dye from aqueous solution using Strychnospotatorum Linn seeds: isotherm and kinetic studies' International Journal of Environment Science and Technology 12:2957–2964.
14. S.Sasikala, G.Muthuraman, (2015) ' Kinetic Studies for Chromium (VI) removal by using Strychnos potatorum Seed powder And Fly ash', International Journal of Science, Engineering and Technology Research (IJSETR), Volume 4, Issue 1.
15. K. Jayaram, I.Y.L.N. Murthy, H. Lalhruaitluanga, M.N.V. Prasad, (2009) 'Biosorption of lead from aqueous solution by seed powder of Strychnos potatorum Linn', Colloids and Surfaces B: Biointerfaces.
16. C. Senthamarai,P. Senthil Kumar, M. Priyadharshini, P. Vijayalakshmi, V. Vinoth Kumar, P. Baskaralingam, K.V. Thiruvengadaravi, and S. Sivanesan, (2012) 'Adsorption Behaviour

of Methylene Blue Dye onto Surface ModifiedStrychnosPotatorum', Environmental Progress & Sustainable Energy (Vol.00, No.00) in AICHe.

17. R. Ajith Kumar, P. Ramamoorthy, V. Sundararaman,K. Jaiganesan, M. Sriram, 'Experimental Investigation on Treatment of Industrial Waste Using Natural Coagulant', International Journalfor Research in Applied Science & Engineering Technology (IJRASET)Volume 6 Issue IV.

18. P. Senthil Kumar (2013) 'Adsorption of Zn(II) ions from aqueous environment by surface modified Strychnospotatorum seeds, a low cost adsorbent' Polish Journal of Chemical Technology.
19. Kumar, P.S., Gayathri, R., Senthamarai, C., Priyadharshini, M., Fernando, P.S.A., Srinath, R., & Kumar, V.V. (2012). Kinetics, mechanism, isotherm and thermodynamic analysis of adsorption of cadmium ions by surface-modifi ed Strychnospotatorum seeds. Korean J. Chem. Eng. 29,1752–1760.