Synthesis, characterizationof the valuable Hydroxysodaliteand its application for remediation of toxic dye:Rhodamine B

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Abstract

Synthesis of valuable Hydroxysodalite(HsL) from the waste fly ash by usingopen hydrothermal method.Synthesized HsLwas characterized using Fourier Transform Infrared spectroscopy, X-ray diffraction, Thermogravimetric analysis, Transmission Electron and Scanning Electron Microscopies. HsLwas applied for remediation of toxic dye, Rhodamine B (RhB) from aqueous solution through method of adsorption. The batch adsorption study such as effect of pH, contact time and effect of concentration on adsorption of RhB on synthesized HsLwas conducted to determinesaturation adsorption condition. After adsorption of RhB on Synthesized HsL were also characterized using Fourier Transform Infrared spectroscopy, X-ray diffraction and Scanning Electron Microscopies. Pseudo second order kinetics and Langmuir adsorption isotherm was well fitted in case of remediation of RhB. Synthesized HsLhave shown more uptake efficiency of RhB dye, which is about 1032.5$\mu g g^{-1}$of HsL at pH 8. Therefore, Synthesized HsLis considered to be efficient and economical adsorbent material for the remediation of RhB.

Key words: Hydroxysodalite, adsorption, kinetics, Fly ash, isotherms.

Introduction

Hydroxysodalite(HsL)is a microporousaluminosilicatepossesses significant physio-chemical properties, which are used as molecular sieving, adsorbent material, catalysis and as ion exchange.In this study the HsL($Na_8[AlSiO_4]_6(OH)_2.2H_2O$)was preparedby open hydrothermal method from wastefly ash [1].HsLis a naturally occurring mineral have flexible structure and geometry that can accommodate variety of cation and have various application such as water softener, as adsorbent, as filler in paint and detergent binder[2-5].HsLconsists of aluminosilicate cage with sodium ion in inter-framework to form a cage structure like zeolite and each unit cell have four β-cage structures[6].

It has molecular sieving effect, adsorption capacity for variety of substances like volatile organic chemical, separation of isomers and mixture of gases, molecular sieving and they are thermally

stable up to high temperature of 1000ºC [7-11]. The synthetic zeolites are painstaking as competitors for natural zeolite. Synthetic HsLfrom fly ash has many advantages over natural occurring HsLin terms of adsorption capacity and higher ion affinity [12,13].

Fly ash is fine powdered containing alumina and silica materialwhich was produced by coal combustion haveCa, Na, Fe, Al, Mg as predominant elements with Cr, Ni, As, Hg, Ba, Zn, Se, as toxic metals[14, 15]. Heavy metal in the fly ash create pollutants in soil and has deleterious effect on natural aqueous body as well as human health during landfill and storage [16, 17].

Approximately 500 million tons of fly ash are produced throughout the year [18]. Fly ash generation is expected to increase in near futureas the demand for electricity increases over years[19, 20]. Fly ashes are abundantly available and according to an estimate, about 125 million ton is generated per year and it will reach 200 million tons in India incoming daysand 6.8 million tons in Malaysia [21, 22]. Production of Fly ash per year of different countries such as India China, USA, Germany, UK, Australia and Canada are 112, 100, 75, 40, 15, 10 and 6 million tons respectively[17, 23](Fig. 1b). Sincecoal is used as the major source of energy, it produces huge amount of fly ash annually [24, 25]. Now a days, fly ash is utilized in preparation of concrete in construction of building and the construction industry produces more than 10 billion tons of concrete annually [26, 27].

Utilization of Fly ash in percentage per year across various countries like India China, USA, Germany, UK, Australia and Canada are 38, 45, 65, 85, 50, 45 and 75 respectively [28, 29], (Fig.1c). More than 80% of the fly ash is disposed as in landfill and ponds, which causes the pollution to atmosphere leading to health problem to living beings [30](Fig. 1a).

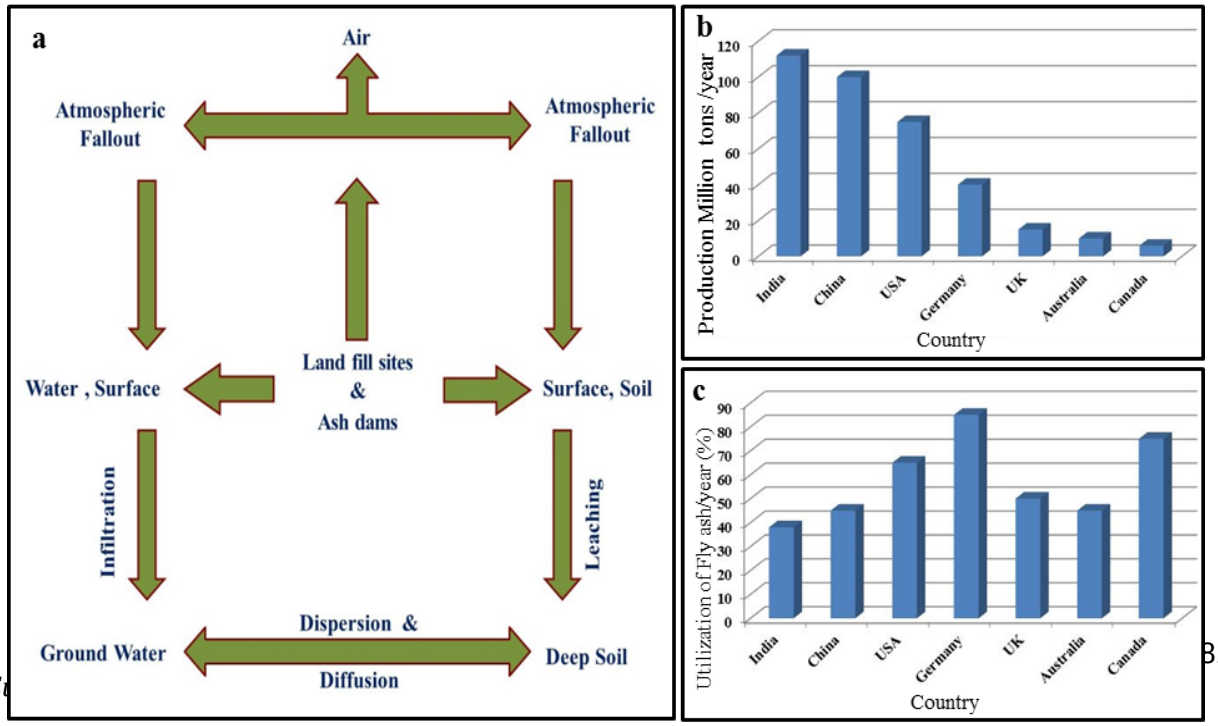


Fig.1. Schematic diagram showing (a) pathways of movement of Fly ash and causing of pollution (b) Globe use of Fly ash per year (c) Globe Production of Fly ash per year

Due to hazardous effect, high production and less utilization of fly ash, it isessentially required to convertthe waste fly ash into the nonhazardous valuable product. Different techniques were in application for conversion of waste fly ash to useful materials,that are organic templatesdepending upon desired shape, structures, pore size of zeolite which contains silica (45-65%), alumina (25-40%)with some amount of heavy metal oxides[31-33].This will reduce the disposal problem of fly ash and will help us to save our nature fromvariety of pollution associated with fly ash.

The synthesized HsLwas tested for its application in remediation of Dye from aqueous solution. Dyes are widely used in the 21st century for various devotions to impact the color into different substances, such as papers, textiles, cosmetics, drugs, color coding, plastic, painting materials etc. [34]. Most of the dyes are organic molecule which is easily soluble in water that leads to the pollution of water bodies and affects the ecosystem. The effluents from the leather and textile industries weredrained out into the natural water bodies, leading to the accumulation of dye materials, which are non-biodegradableorganic materials.

The synthetic dyes are majorly health hazard in nature and it is also difficult to regeneratethe dissolve oxygen in water bodies once it is polluted with dyes [35].Because of above reasons, remediation of dyes molecules is paramount important. There are various methods using for remediation of dyes such adsorption, precipitation, electro-kinetics coagulation, reverse osmosis, photo oxidation that are usually applied for the detoxification of dye molecule present in the wastewater. Out of them adsorption method is considered to be simple and economically viable for the remediation of toxic dye from waste water.A variety of adsorbent material such as biodegradable waste, naturally occurring clay material, carbon nanotubes, metal organo-framework,nano-metal oxides and agricultural wasteare utilized in extraction of dyes etc. [36].In the present work, synthesized HsLwas applied for remediation of RhB dye.This dye is fluorescent, cationic in nature that used in textile as colorant, in foodstuffs and in pharmaceutical industries [37]. RhB is neurotoxic in nature for human as well as animal or other living being and

it also causes skin and eye damage and gene mutation too [38].Since RhB dye are not degradable in the pH range of 6 to 8 and the most polluted water resources also have this pH range [39].

Experimental

Materials

Sodium Hydroxide, AR grade was purchased from Merck private limited Germany. Fly ash was collected from the National thermal power plant NTPC (India). Organic Dye Rhodamine B is cationic dye. C.I. Number C754170, molecular weight 479.02 and molecular formula $C_{28}H_{31}ClN_2O_3$ was perches fromMerck private limited. HCl, KCl, NaOH and $KH_2PO_4$was procured from Thomas Baker Pvt. Ltd. Other analytical grade chemicals/reagentswere used without any purification. All the reactions were done in double distilled water.

Technique

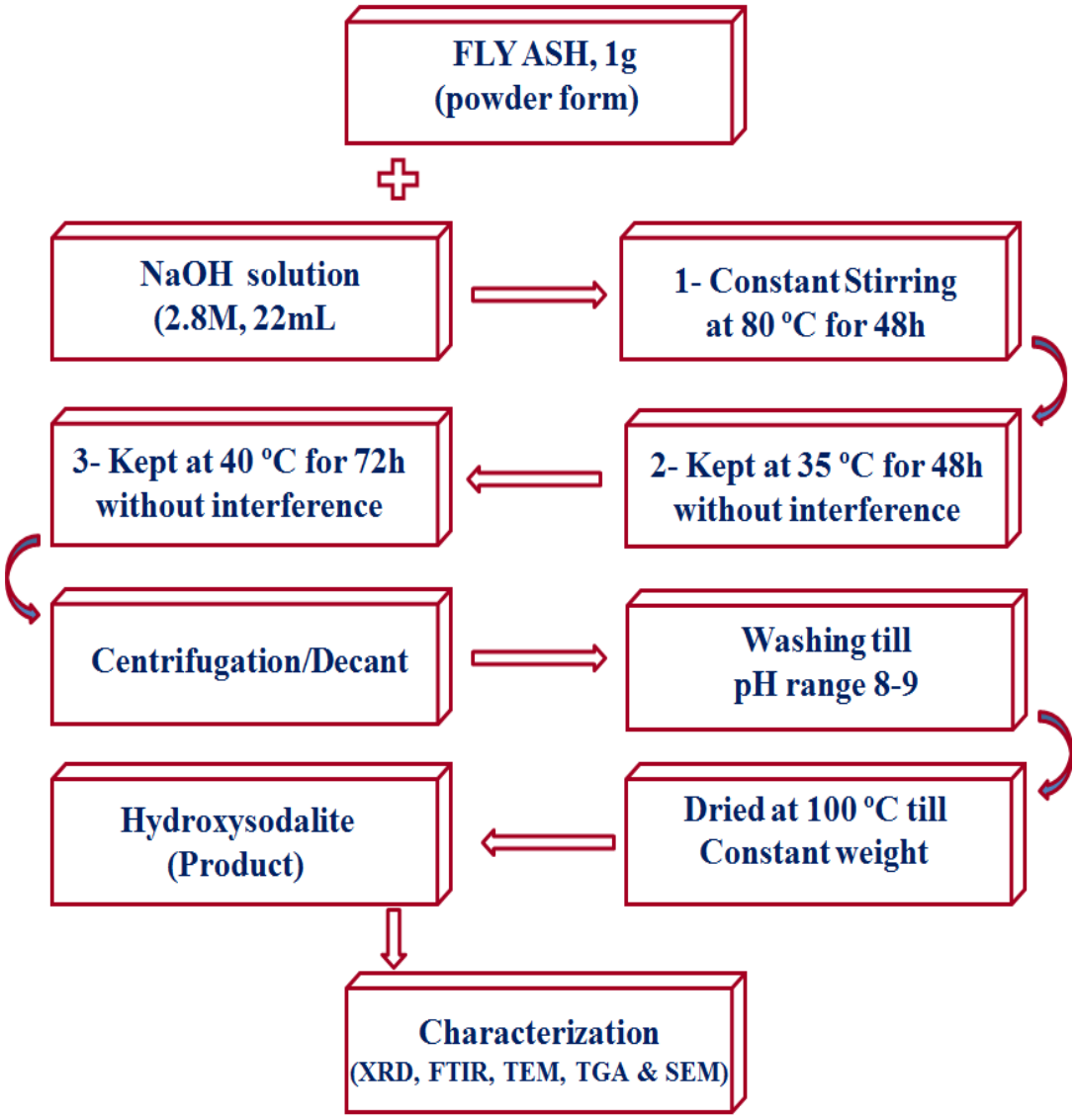
Power X-ray diffraction(PXRD) pattern were recorded between 2 to 70º (2θ) with X-ray Diffractometer (D8 DISCOVER BRUKER AXS, Germany) at 40kV and 30mA.Fourier Transform Infrared spectroscopic (FTIR) study was conductedby Spectrum RXI Mid IR Perkin Elmer. Thermogravimetric analysis (TGA)was recorded using Perkin-Elmer system and Transmission Electron Microscopic assessment (TEM) was performed using TECNAI G2T30FEL and Scanning Electron Microscopic (SEM) analysisby using JEOL JSM-6610LV.

Synthesis of Hydroxysodalite

Fly ash was used as the constituent of alumina (25-40%) as well assilica (45-65%) for preparation of framework aluminosilicates (Hydroxysodalite).HsL hasthree-dimensional open crystal structures, variable pore size(Fig. 2).

fig. 2. Two dimensional Structure of Hydroxysodalite

They are more hydrophilic in nature. The HsLwas synthesized through two step hydrothermal technique. 1 (one)g of fly ash was first taken in a 100 ml conical flask and 22ml of 2.8M NaOH solution was added into it.The reaction mixture was maintained at 80ºC with constant stirring on a magnetic stirrer for 48 h by open hydrothermal process, a suspension of brownish color was obtained.Then, reaction mixture was further kept at 35°Cfor 48 hrs. and at 40 ºC for 72 hrs.without interference.



Scheme 1. Schematic representation of methodology for synthesis and characterization of HsL

The supernatant was decanted from the reaction mixture. The residue product was washed with double distilled water several times till the filtrate's pH becomes neutral. The precipitate obtained was dried at 100 ºC in an oven to have constant weight. The synthesized product was characterized by standard characterization techniques as represented in Scheme 1.

Result and discussion

Estimation of RhBdye in solution

Adsorption studies of RhB dye on synthesizedHydroxysodalite was performed with variation of pH of RhB dye solution to show its effect on adsorption, contact timefor batch adsorptionas well as concentration of the RhB solution. Percentage adsorption of RhB dye on the HsL was calculated by usingfollowing equation.

$$\%\ \boldsymbol{Adsorption\ of\ dye} = \frac{Initial\ concentration\ of\ dye - Final\ concentration\ of\ dye}{Initial\ concentration\ of\ dye} \times 100$$

Calibration plot for quantitative assessment of RhBdye

A 250 ppm solution of RhBdye was made in a 500 mL volumetric flaskas a stock solution and subsequently the solutions of 1, 2, 3, 4, 5 ppm were made through dilution from the stock solution. The absorbance value was recorded for each of the solution and the calibration plot was prepared with adsorption versus concentration for further calculation that involved in the experiment. Accordingly, the λ_{max}ofRhB dye was found to be at556 nm (Fig 3a) in the aqueous solution. Since RhB dye in aqueous solution is more stable in pH range of 4 to 12 due to this all theestimation of dyeby UV-Visible spectroscopy was performed at pH 7[39,40].

Batch adsorption Studies with HsL

In Batch adsorption studies, pH effect of dye solution on adsorption of RhB on synthesized HsL was tested. Twelve set of conical flask, each have 25 ml of 25ppm of RhBsolution having pH of 1to12 with constant concentrationwas allowed to interact with 20 mg of HsL for 10 minutes. The percentage adsorption/uptake was measured as a function of pH of solution and percentage uptake at pH 1 and pH 5 were found to be 75.64 and 77.21 respectively. The highest percentage adsorption of 82.3 % was found at pH 8depicted in Fig 3b. In the basic medium HsL is stable

and adsorptive site of adsorbent is more active. Accordingly, pH 8 was chosen for further estimation of RhB with different studies.

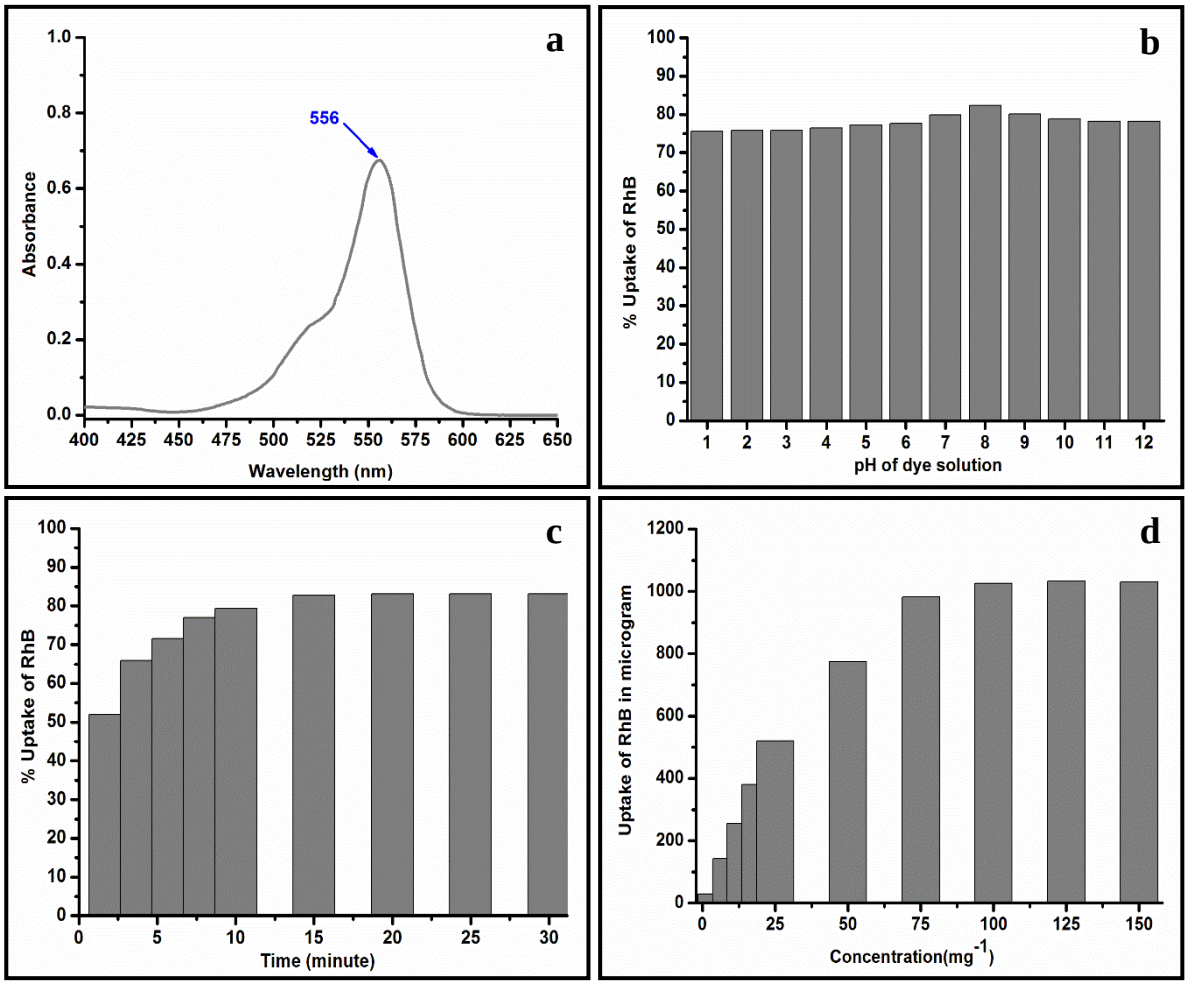


Fig.3.(a) Absorbance value of RhB dye (b) % Uptake of RhB as function of pH (c)%Uptake of Dye as function of contact time (d) Uptake of RhB as function of its concentration

In case of percentage adsorption /uptake as a function of contact time, in which time used to take 2, 4, 6, 8, 10, 15, 20 25 minute interval and performed up to 30 minutes(Fig 3c). Percentage adsorption of dye ss very fast and was found was found to be 51.96 within 2 minutes and it increases up to 83.14 in 20 minutes,and it becomes saturated after 20 minutes due to all vacant adsorptive site being filled on synthesized HsL. This contact time i.e.; 20 minutesand pH 8 was accordingly decided for further adsorption studies. After that we have studied Percentage

adsorption of RhBdye as a function of concentration in which took different concentrations of RhB dye solution such as 5ppm, 10 ppm, 15 ppm, 20ppm, 25ppm, 50ppm, 75ppm, 100ppm, 125 ppm 150ppm (Fig 3d) at pH 8 and for saturation time 20 minutes with 20 mg of HsL. Percentage adsorption/Uptake of RhBdye was found to be 141.91 μg and 775.74 μg at 10 ppm and 50ppm, respectively. The highest uptake of 1032.48 μg was found at 125ppm concentration of RhB. This composition was characterized by various techniques for interpretation of interaction between synthesized HsL with RhBdye molecule.

Adsorption Isotherm studies

Adsorption isotherm is a mathematical model which describes the distribution of adsorbates molecule among the adsorbent and liquids. Based on assumptions andhomogeneity/heterogeneity of the adsorbents,the possible nature of interaction between adsorbates and adsorbent molecule was explained. Langmuir and Freundlich adsorption isotherm model were discussedin adsorption isotherm studies [41-46].

Freundlich isotherm model explains about the importance properties of the heterogeneous surface, reversible adsorption and formation of more than two layers on adsorbent surface. Equation 1is the linear equation of Freundlich adsorption isotherm model. The Plot of log q_e versus log $C_e$was linear with the slope of 1/n and K_f, the intercept (Fig 4b). The value of slope (1/n) indicates strength of adsorption process that is, 1/n <1 is the indicative of normal adsorption and 1/n >1 indicates the cooperative adsorption. When 1/n =1, it means independent concentration that is partitioned between two phases.

$$\mathbf{Log q_e = log K_f + 1/n \, log C_e} \quad \textbf{(Equation 1)}$$

Langmuir adsorption isotherm model gives the idea of mono layer formation adsorbent surface.Equation 2 is the linear form of Langmuir adsorption isotherm. Plot between $\log C_e/q_e$ versus log $C_e$gives the linear(Fig 4a). In this equation,the capacity of adsorbent (mg/g) is represented by q_{max} and the adsorption constant (dm^3/mg) by K_L, its slope by $1/q_{max}$ and the intercept by $1/(q_{max} K_L)$. Separation factor referred to the Langmuir is represented by R_L defined by Webber [47]which is represented in Equation 3.

Magnitude of R_L indicates relative affinity between the both adsorbates and adsorbents. The phenomenon of adsorption was obtained from R_L values. If R_L value is equal to 1, which

indicates linear, the favorable adsorption is indicated by the value of $R_L$between 0 to 1 and the value of R_L greater than 1 represents unfavorable adsorption.

When it is equal to zero, it indicates irreversible adsorption. R_L values are calculated at all the possible concentration and its value less than one indicates favorable adsorption, the plot between R_L versus concentration (Fig.5d).

$$C_e/q_e = 1/(q_{max}K_L) + C_e/q_{max} \quad \textbf{(Equation 2)}$$

$$R_L = 1/(1 + K_L C_i) \quad \textbf{(Equation 3)}$$

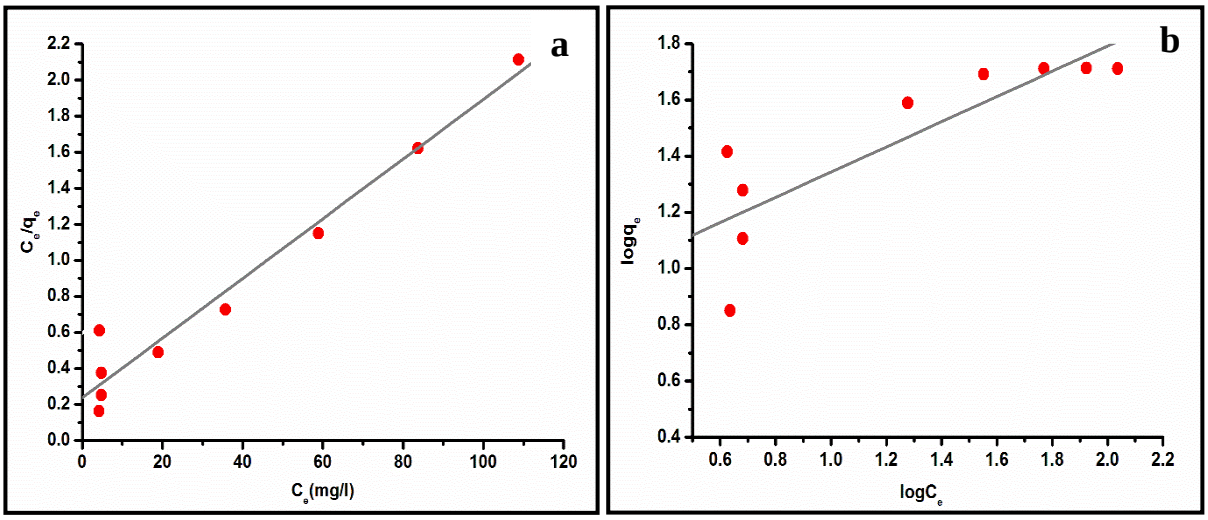


Fig.4.(a) Langmuir Absorption isotherm and (b)FreundlichAbsorption isotherm

The Langmuir and Freundlich's constant parameters werearranged in Table 1. The best fitted isotherm was indicated by the correlation coefficient (R^2) of the plots. SinceR^2 = 0.9596 in Langmuir isotherm in comparison to Freundlich isotherm where it's R^2= 0.7254, so, it follows Langmuir adsorption isotherm model.

Table 1. Parameters constant ofFreundlich Absorption isotherm and LangmuirAbsorption isotherm

Freundlichisotherm constants				Langmuir isotherm constants			
1/n	n	K_f (mg g^{-1})	R^2	q_{max} (mg g^{-1})	K_L (dm^3mg^{-1})	R_L	R^2
0.4485	2.2296	7.8415	0.7254	60.2409	0.0703	0.1021	0.9596

Kinetics studies

Various kinetics models in term of pseudo first, second order and intra particle diffusion were studied to examine the controlling mechanism of adsorption process. Pseudo first order kinetics model describe adsorption rateaccording to capacity of adsorption [48]. The pseudo first order kinetics modelis represented in equation4. The straight line was obtained when the plot is made between log (q_e-q_t) and t. Its slope is represented –K_1/2.303 and the intercept by logq_e(Fig.5a).

$$\log(q_e - q_t) = \log q_e - (K_1/2.303)t \quad \textbf{(Equation 4)}$$

In this equation,q_e represents amount of dye adsorbed at time t and q_t, amount of dye adsorbed at equilibrium. K_1 represents rate constant.

Pseudo second order kinetics model was described by Ho and McKay for determination ofkinetics of adsorption[49].The equation5 represents the linear equation of pseudo second order. A straight line is obtained by plotting t/q_tversus t with slope of $1/q_e$ and intercept,K_2qe^2(Fig. 5b).

$$t/q_t = 1/K_2q_e^2 + (1/q_e)t \quad \textbf{(Equation 5)}$$

Intra particle Diffusion is other kinetics model which was described by Weber and Morris for determination of the rate of adsorption of adsorbates molecule on adsorbent [50].Linear form of the Intra particle Diffusion kinetics model is shown in Equation-6. The plot between q_t versus $t_{1/2}$ gives a straight line which has the slope,K_d and intercept, C (Fig. 5c).

$$q_t = K_d t^{1/2} + C \quad \textbf{(Equation 6)}$$

The constant parameters of various kinetics models were given in Table2**.** The correlation coefficient (R^2) of Pseudo second order kinetics is 0.9950 that is well fitted as compared to Pseudo first order model (R^2 = 0.6813) and Intra particle diffusion model (R^2 = 0.7413). So, this means that pseudo second order kinetics is followed.

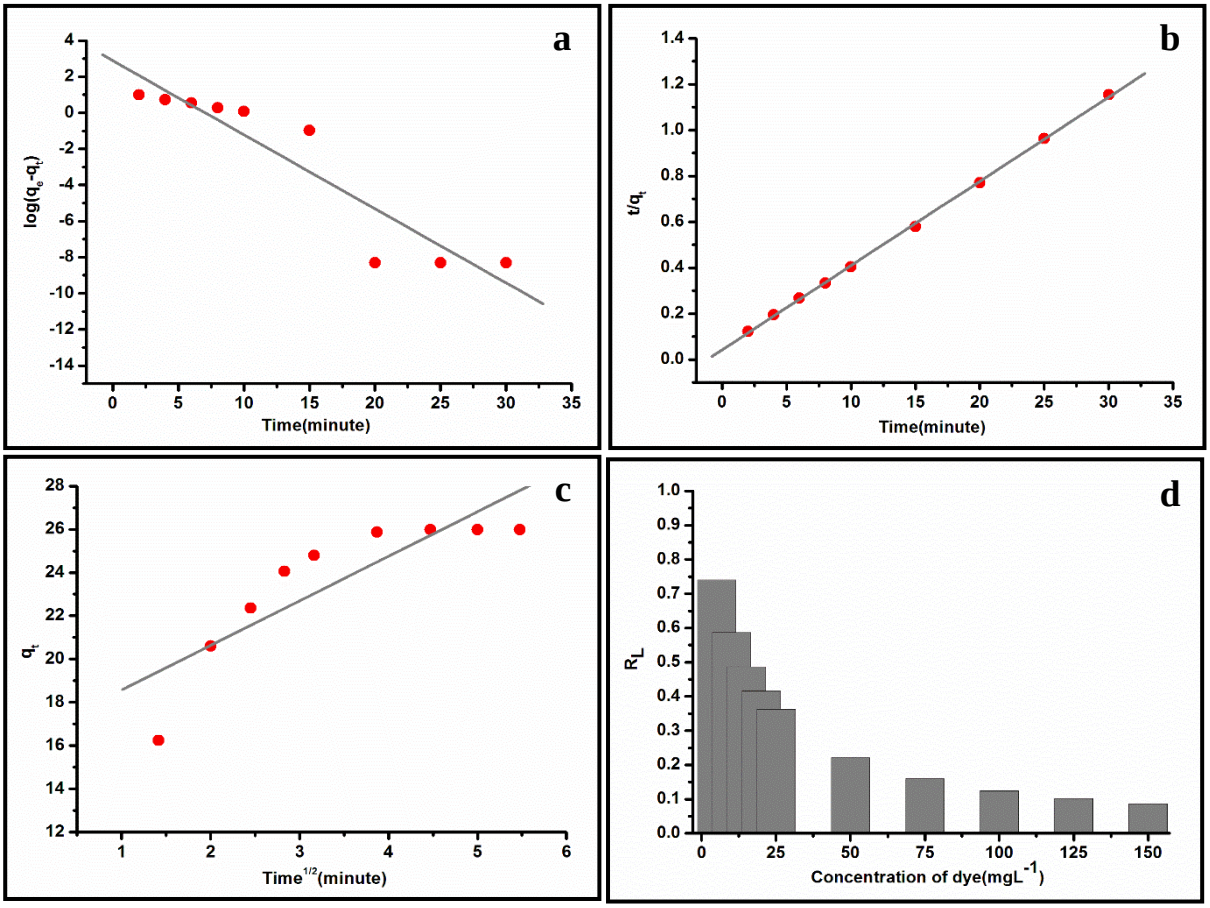


Fig.5. (a) Kinetics studies such as Pseudo first order (b) Pseudo second order (c) Intra particle diffusion and (d) R_L value

Table 2. Parameters constant of various kinetics models

Pseudo-first-order model			Pseudo-second-order model			Intraparticle diffusion model		
K_1	q_e	R^2	K_2	q_e	R^2	K_d	C	R^2
0.0610	3.6906	0.6813	0.0294	7.4239	0.9950	2.0619	16.513	0.7417

Characterizations

FTIR analysis

Fourier Transform Infrared spectrumsof raw fly ash and the synthesized aluminosilicate (Hydroxysodalite) and RhB adsorbed HsLwererecorded by Spectrum RXI Mid IR Perkin Elmer in the region 400-4000 cm^{-1}(Fig. 6 and Fig. 7). In IR spectrum of raw fly ash, the presence of

quartz and mullite was shown by the peaks at 1095 cm^{-1} and 905 cm^{-1}[51-54]. The peaks at 562 cm^{-1} and 468 $cm^{-1}$is attributed to the presence of Si/Al ratio and tetrahedral unit (TO_4^{-4}) in raw fly ash [55] (Fig. 6a).

The vibration bands at 429 cm^{-1} and 460 cm^{-1} appears in the spectrum of aluminosilicate (Hydroxysodalite)is linked to the band of absorption of the single four memberring (S4R) and the bending band of O-T-O of the tetrahedron units (TO_4^{-4})(Fig. 6b). The adsorption bands in the region of 900-1200 cm^{-1}, 550-800 cm^{-1}, 540-640 cm^{-1} and 400-500 cm^{-1}areattributed to the presence S4R group resembling of zeolite [56].

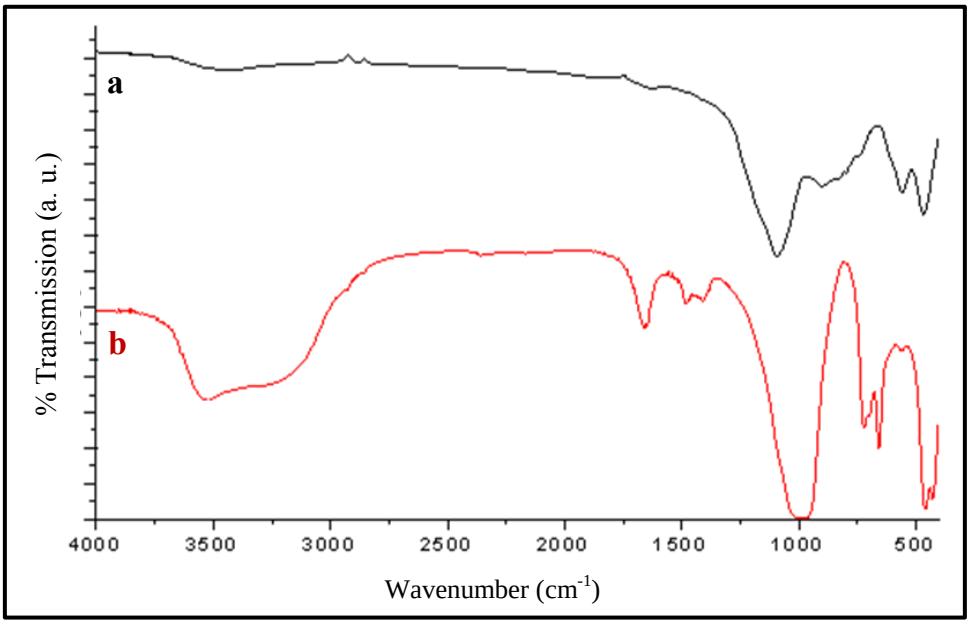


Fig.6.FTIR spectrums (a) Raw Fly ash (b) synthesized Hydroxysodalite

In the analysis of spectrum of adsorbed aluminosilicates, there is decrease in the peak in comparison to fly ash at the peak, 562 cm^{-1} that means the dissolution of some amount of silica out of fly ash on formation of gel and that was decanted on washing of the product to reduce pH of the product. The symmetric and asymmetric stretching bands of T-O-T bond appeared at 659 cm^{-1}, 702 cm^{-1} and 988 cm^{-1} [57, 58]. The additional absorption bands at 1411 cm^{-1} and 1480 cm^{-1} appeared in the spectrum of the product is corresponding to CO_3^{-2} molecule trapped in the cavity of the hydroxysodalite [59, 60] and the absorption bands at 1661 cm^{-1} and 3280

cm^{-1} corresponds to the bending and stretching vibration band of Zeolitic water molecules of aluminosilicate. The additional bands appeared at 3533 cm^{-1} is because of Al-OH stretching bands of aluminosilicate. The frequencies of vibration appeared in spectrum of prepared product are similar to that of natural hydroxysodalite.

In case of RhB adsorbed Hydroxysodalite, there is additional adsorption band around 1411 cm^{-1} corresponding to -CH_2 scissoring vibration of RhB. The peaks at1345 cm^{-1} and 1472 cm^{-1} are due to CH vibration and 1600 cm^{-1} corresponds to C=O group of RhB. Absorption bands at 1647 cm^{-1} is because of H_2O bending vibration and the broad peak at 3369 cm^{-1} is due to presence of adsorbed and bonded water

The peak at 978 $cm^{-1}$is linked to the presence of Al-O-Si stretching bands of Hydroxysodalite. Presence of additional peaks of RhB dye in comparison to synthesized hydroxysodalite indicates adsorption of RhB on hydroxysodalite (Fig.7).

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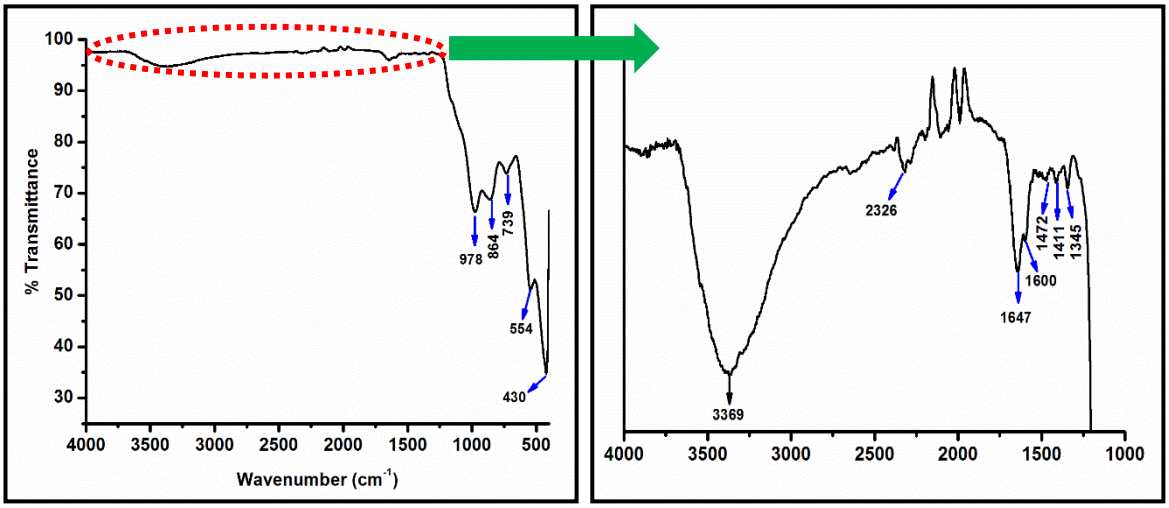


Fig. 7. FTIR spectrum of RhB adsorbed onHydroxysodalite

XRD analysis ofHydroxysodalite

Power X-ray diffraction (PXRD) pattern of raw fly ash and the synthesized aluminosilicate (Hydroxysodalite) wererecorded between 6 to 70º (2θ) by X-ray Diffractometer (D8 DISCOVER BRUKER AXS, Germany) at 40kV and 30mA (Fig. 8).

In the XRD pattern of fly ash,the diffraction angle 2θ values are found to be 16.37, 20.87, 26.29, 31.04, 33.22, 35.31, 36.92, 39.23, 40.98, 42.58, 54.14, 57.72, 60.84 and 64.66. Broad hump around 26.29 and sharp intense peaks indicate that there is a mixture phase of amorphous and crystalline in fly ash(Fig. 8a).

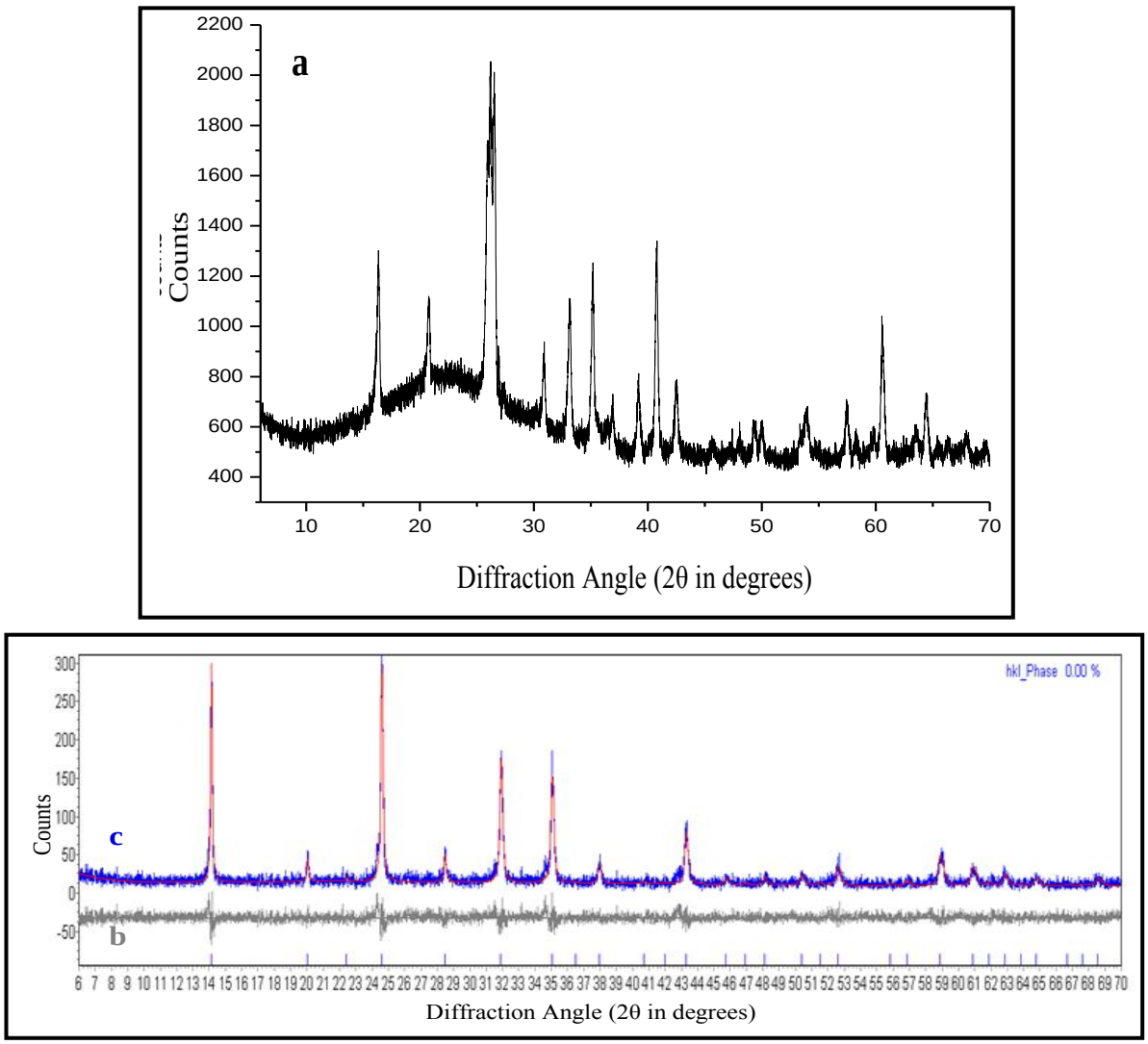


Fig.8.(a) XRD pattern of raw fly ash(b) vertical line on 2θ values denote the JCPDS-ICDD peak position (c) synthesized HsL

In case of synthesized HsL,diffraction angle 2θ value are found to be 14.06, 20.06, 24.56, 28.60, 31.96, 35.19, 38.08, 43.51, 45.82, 48.13, 50.66, 52.85, 57.03, 59.22, 61.18, 63.04, 65.00 and 68.93 (Fig. 8c). The synthesized product was analyzed with the help of Topas software Disappearance of peaks in fly ash and reappearance of new sharp and intense peaks indicates the

formation of new framework aluminosilicate. In the synthesized product, 2θ positions for the diffraction peaks fit precisely to the $Na_4Al_3Si_3O_{12}(OH)$ composition cited by JCPDS-ICDD file No. 11-0401 (Hydroxysodalite phase with space group P-43n(218) in JCPDS-ICDD data) [61].(Fig.8b). The unit cell length of the product was calculated by analytical method using XRD 2θ values.

The relative intensities of the peaks in the synthesized product differ from that of naturally occurring HsL indicating difference in the Si/Al ratio. An increase in the unit cell length of the synthesized product from that of naturally occurring HsLindicates decrease in the Si/Al ratio or crystal defect due to the presence of impurities in the synthesized HsL. The peak positions in the synthesized product were found to be in good agreement with the peaks of Hydroxysodalite.

TGA analysis ofHydroxysodalite

Thermogravimetric analysis (TGA) pattern of the synthesized HsLwere recorded between 30 to 750 ºC by TECNAI G2T30FEL (Fig. 9). Synthesized HsL shows four stages of weight losses between 30 to 750 ºC i.e.; first weight loss between 30 to 147.17ºC is 5.12%that indicatesmoisture losses, Second weight loss between147.17ºC to 237 ºCis 5.55 % which is due to desorption of physically adsorbed water out of micropores,third weight loss between 237 ºC to 286.29 ºC is 2.19% that is considered to be linked to loss of water out of hydration complexes formed with exchangeable cation[62] andfourth weight loss in between286.29 ºC to 750 ºC is of 1.67% which is due to dehydroxylationand destruction of hydroxyl bonds formed [63].

TGA curve of the synthesized compound shows total weight loss of 13.59% from 37.49 ºC to 627.78 ºC (Fig. 9a). The DTA curve shows two endothermic peaks, the first endothermic peaks at 147.3 ºC corresponding to the dehydration of the adsorbed surface water molecules and second, endothermic peak at 236 ºC corresponding to the dehydration of Zeolitic water molecules (Fig. 9b).

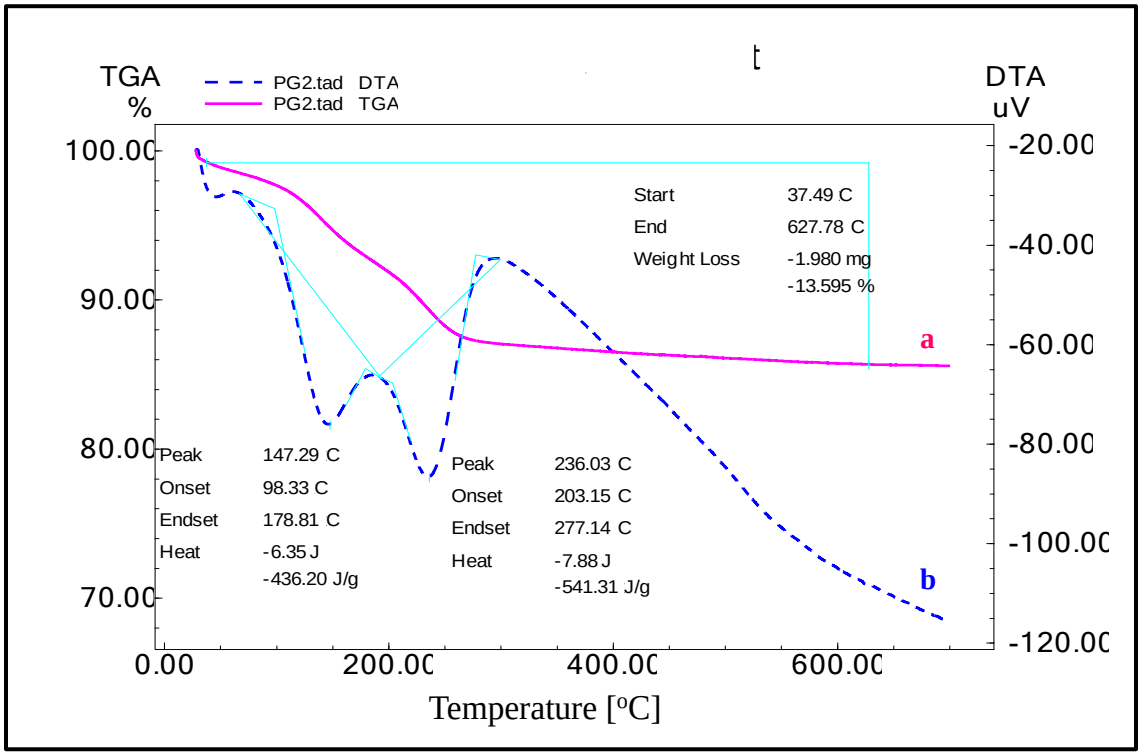


Fig.9. Smooth line represents the TGA curve (a) and dotted line, the DTA curve (b) of synthesized hydroxysodalite

SEM and TEM analysis ofHydroxysodalite

Scanning Electron Microscopic (SEM) and Transmission Electron Microscopic (TEM) imageof synthesized HsLwere recorded using JEOL JSM-6610LV and TECNAI G2T30FEL respectively (Fig.10,Fig.11).SEM of the RhB adsorbed hydroxysodalite(Fig. 12).

The SEM image of synthesized HsL shows unique hierarchical spherical and disc-like platelets. Size of the disc-like platelets is in the range of 40 nm to 90 nm (Fig. 10a to 10c). EDS analysis of the synthesized aluminosilicate indicates negligible amount of heavy metals such as Fe, Ti, Mg, Ca and Cr etc.. The atomic ratio of Si/Al in the synthesized product calculated from EDS is slightly less than unity (Fig. 10d). TEM images show unique hierarchical spherical and slightly cubical platelets of synthesized HsL. Size of the spherical platelets is in between 50 nm to 180 nm (Fig. 11a to 11e).

The shapes of the nano size crystal are observed to be cubical. EDX confirmed that synthesized product is alumina rich rather than silica-rich and presence of some heavy metal ions, such as Fe,

Ti, Mg, Ca that might have replaced silicon atoms in the frame work structure. Presence of bright spots in diffraction pattern indicates the product as crystalline in nature (Fig. 11f).

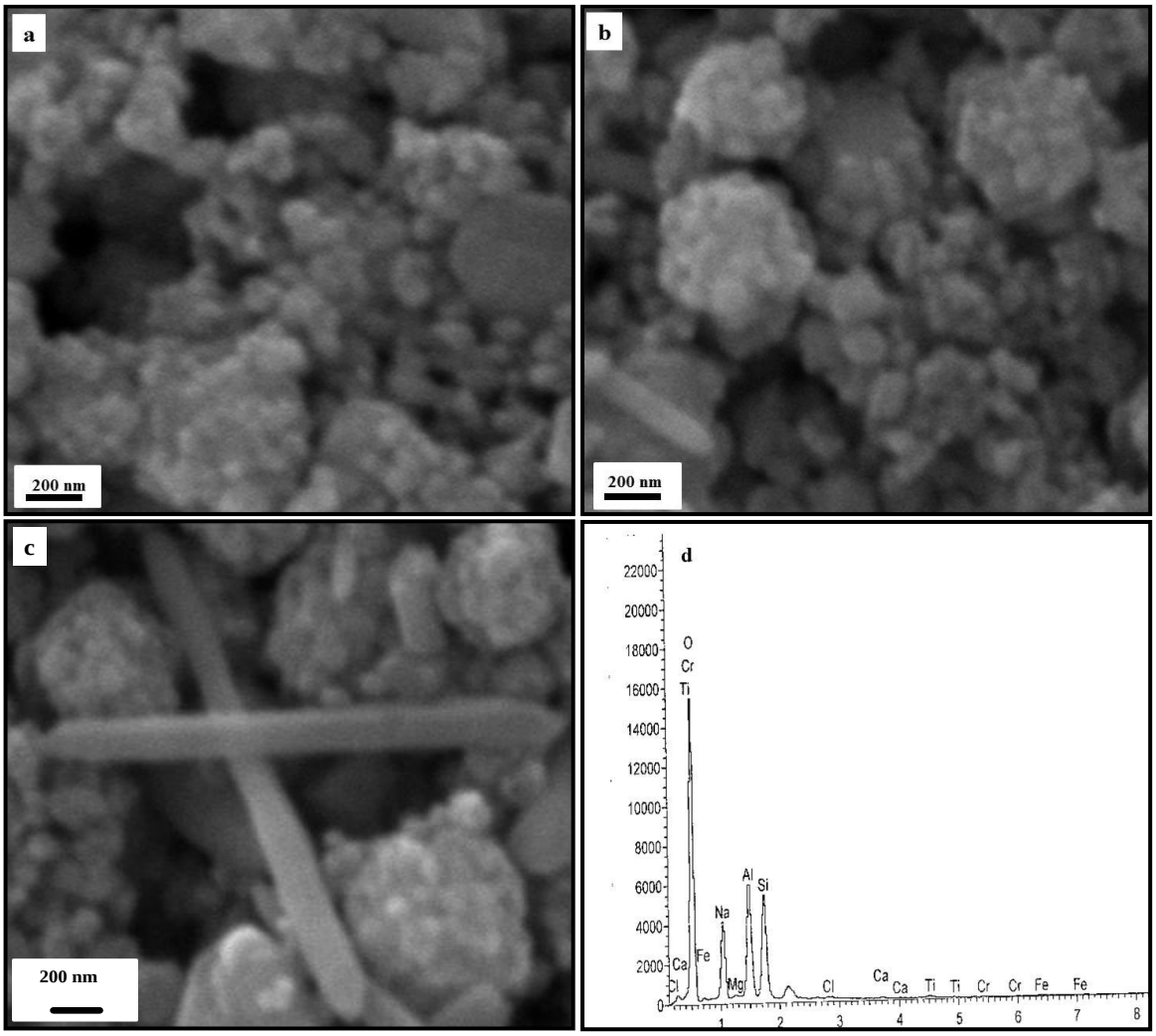


Fig.10. (a), (b) & (c) SEM images of synthesized HsLwith different magnification and (d) EDS plot of synthesized HsL

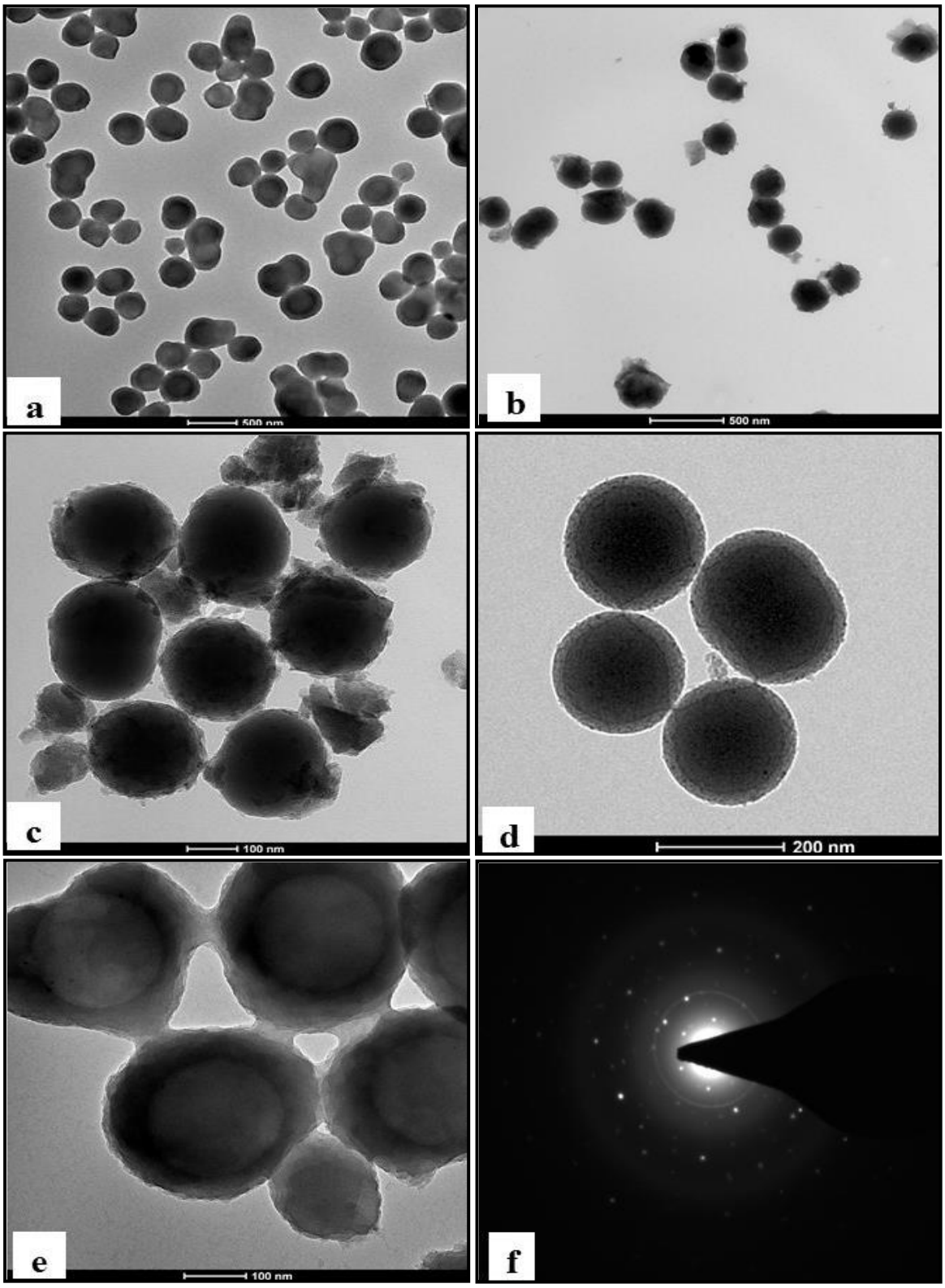
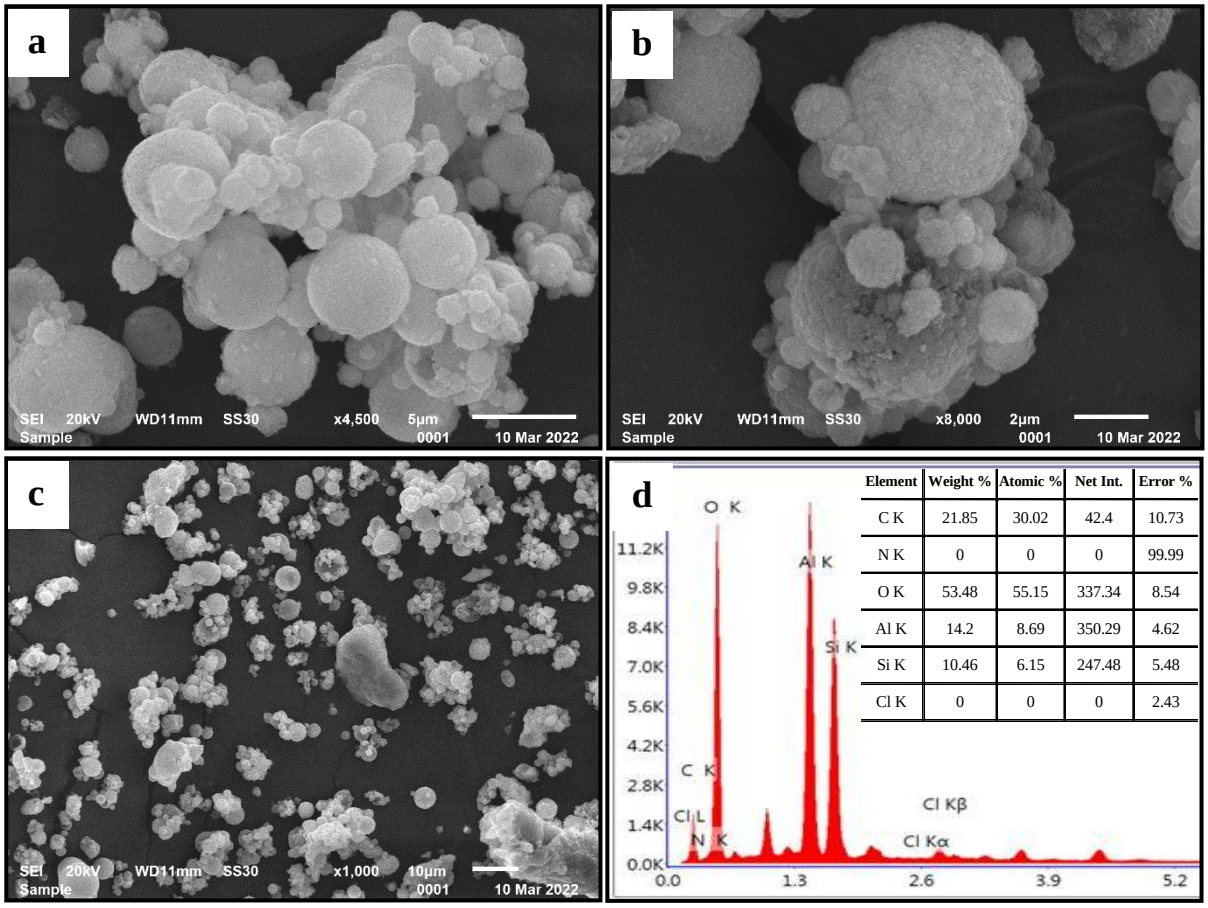


Fig.11.(a). (b), (c), (d) & (e) TEM images of synthesized HsLwith different magnification and (f) EDX pattern of synthesized HsL

The SEM image of RhB adsorbed on HsL was relatively smooth as compared to that of pristine HsL. Size of the RhB adsorbed on HsL is in between 2 to 4 μ with spherical shape (Fig. 12a-12c). In case of EDS analysis of the RhB adsorbed on HsL shows the presence of heavy metals such as C, N, O, Al, Si, etc. The presences of Carbon peak (from RhB dye) indicates RhB dye adsorbed on hydroxysodalite (Fig. 12d).



Element	Weight %	Atomic %	Net Int.	Error %
C K	21.85	30.02	42.4	10.73
N K	0	0	0	99.99
O K	53.48	55.15	337.34	8.54
Al K	14.2	8.69	350.29	4.62
Si K	10.46	6.15	247.48	5.48
Cl K	0	0	0	2.43

Fig. 12.(a), (b) & (c) SEM images of RhB adsorbed on HsL(d) EDS plot of elemental composition present in RhB adsorbed on HsL

Interaction of RhB dye with HsL in adsorption

In the adsorption process, HsL has some adsorptive site that interacts with RhB dye, possible schematic diagram of mechanism of interaction between HsL with RhB(Fig.13).RhB dye adsorbed on the surface of HsL due to because of electrostatic interaction and some molecule are also trapped inside the pores of HsL[64, 65].

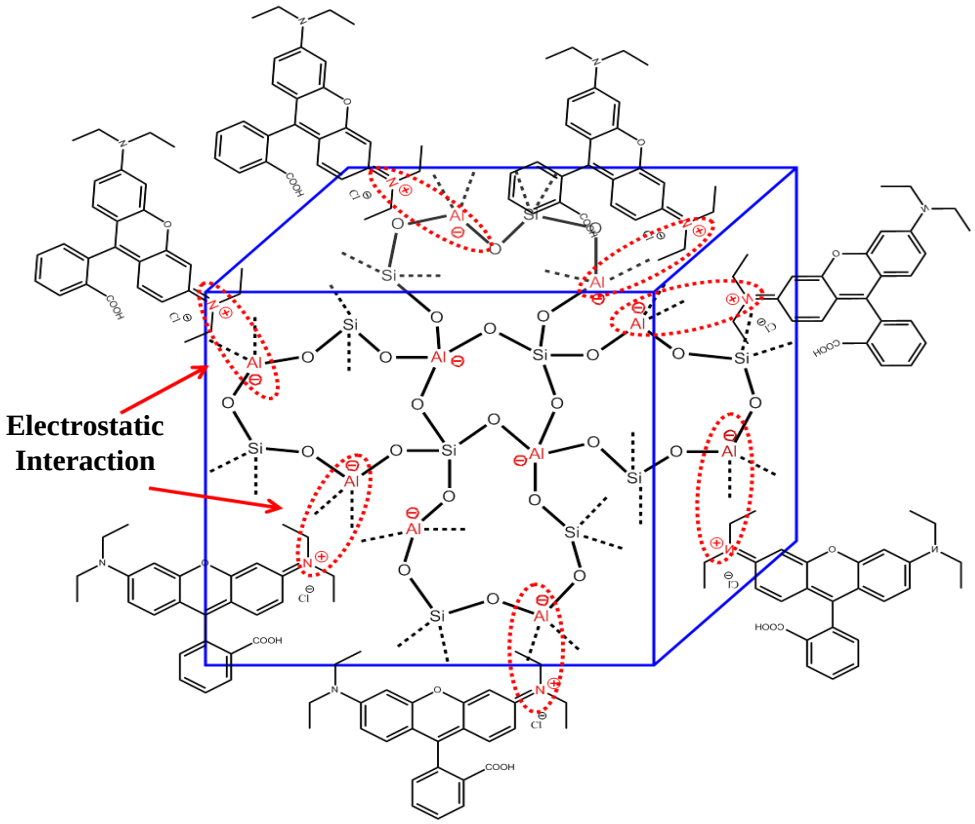


Fig.13. Schematic diagram of interaction between HsL with RhB

Conclusion

The synthesis of HsLby hydrothermal method from waste fly ashwas successfully performed in two step process and the synthesized products were characterized by TEM, SEM and FTIR. Unique hierarchical spherical and disc-like platelets with size of 40 nm to 180 nm were displayed in SEM and TEM images. TGA curve of synthesized compound shows total weight loss of 13.59% from 37.49 ºC to 627.78 ºC. The peak positions of XRD and FTIR in the synthesized product were found to be in good agreement with the peaks of HsL.Adsorption parameters of dye adsorbed on HsLobserved frombatch studies adsorption isotherms and kinetics models reveals that the process involved follows Langmuir adsorption mechanism and kinetic of Pseudo second order. The highest remediation of RhB was found to be 1032.48µg at 125 ppm concentration, and R_L value less than 1 confirms the involvement of favorable adsorption process. It is also observed that the interaction between the dye and HsL is of electrostatic in

nature with trapping of molecules inside the pores of HsL. Therefore, the synthesized HsLis a potential material in remediation of RhB dye out of aqueous solution.Therefore, it is concluded thatthe study is significance for restoration of the natural resources like water, air and agricultural lands from pollution of fly ash as well as from RhB dye.

Conflict and Interest

There is no conflict of interest regarding manuscript that is declared by the authors.

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