SYNTHESIS AND CHARACTERIZATION OF THIOL FUNCTIONALIZED MESOPOROUS ZIRCONIA AND ITS UTILIZISATION FOR THE REMOVAL OF METHYL BLUE FROM WASTE WATER

A

Dissertation

Submitted in Partial fulfillment for the Award of the Degree

Master in Science

In

CHEMISTRY

By

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Roll No: 412CY2020

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Under the Supervision

of

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DECLARATION

I **Miss. Supriya Priyadarshini**, NIT, Rourkela declare that all my research works are original & no part of this thesis has been submitted for any other degree or diploma. All the given information & works done are true to my sense & knowledge.

(Supriya Priyadarshini)

Date:

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We owe our cordial gratitude to my respected teacher and supervisor **Prof. R. K. Patel**, Department of chemistry, National Institute of Technology, Rourkela, whose splendid guidance, authentic supervision, assiduous cooperation, moral support and constant encouragement enabled me to make out research problem in the present form. I am thankful to all the faculties of our department for their cooperation and help.

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Lastly I express my abysmal adoration & heartfelt devotion to **my beloved parents** for their countless blessings, unmatchable love, affection & incessant inspiration that has given me strength to fight all odds & shaped my life, career till today. In the end I must record my special appreciation to **GOD** who has always been a source of my strength, inspiration & my achievements.

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CERTIFICATE

*This is to certify that the dissertation entitled "**Synthesis and characterization of thiol functionalized mesoporous zirconia and its utilization for the removal of methyl blue from waste water**" being submitted by Supriya Priyadarshini, Roll number 412CY2020, Department of Chemistry, National Institute of Technology, Rourkela, for the award of the degree of Master of Science is a record of bonafide research carried out by her under my supervision and guidance. To the best of my knowledge, the matter embodied in the dissertation has not been submitted to any other University/Institute for the award of any Degree or Diploma.*

The present study is a valuable contribution for the advancement of knowledge in the field of material chemistry and its environmental application.

NIT Rourkela — Prof. R. K. Patel

Date: — (Supervisor)

CONTENTS

Chapter-1

1. Introduction

Materials having mesostructure are characterized by its pore dimensions which is midway between micro and macro-levels. A mesoporous material[2] is a solid porous material containing pores with diameters between 2 and 50 nm. Porous materials are classified into several types based on their magnitude. According to IUPAC notation, the pore widths things of microporous material have less than 2 nm and macroporous materials have hole distances of greater than 50 nm; the mesoporous materials thus deceits in the middle. The finding of porous material has led to a new field of study which has a wide application. Porous materials have been a new field of interest for the researchers due to its large surface area, well-defined structures and large pores. Typical mesoporous materials include some kinds of silica and alumina that have similarly-sized fine mesopores. Mesoporous oxides of niobium, tantalum, titanium, zirconium, cerium and tin have also been well documented. Well-ordered mesoporous materials (OMMs) are considered as better sorptives material but that may be misused owing to their large seeming areas (typically 200–1000cm^2 g^{-1}) and large pore dimensions.

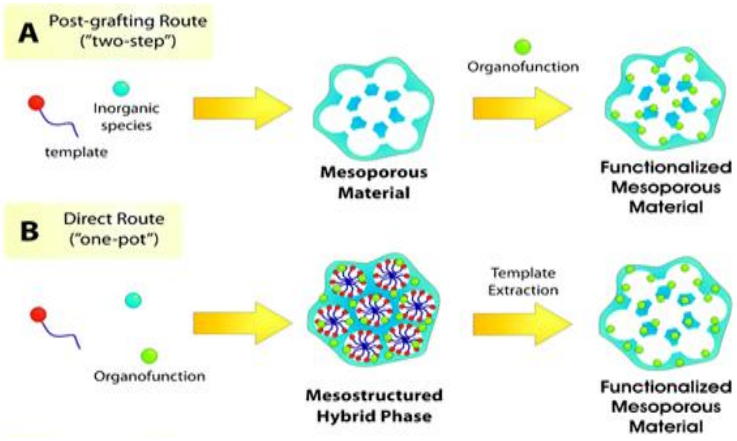
Many researchers have focused organically functionalized adsorbents such as organo clays[3], polymer nano composites[4], functionalized silica gel[5,6] and so on. Over the past two decades, organo functionalized mesostructured silicas have established as a promising sorbents and have generate a wide ground of requests. These functionalized silicas can successfully be used as adsorbents for the elimination of several toxic metal ions and other dangerous chemicals for ecological clean-up requests.

1.1 Literature Review

Most of the earlier described mesoporous zirconia materials produced through surfactant pathway[7] own amorphous structure, and in many cases, these materials undertake corporal collapse of their structure on high-temperature crystallization/calcination which could significantly bound their functional applications in adsorption and catalysis. Herein, some researchers report the synthesis of ca. 7.0 nm sized zirconia nanocrystals, using F127 as template, and their self-assembly toward mesoporous ZrO_2 structure. Further, the mesoporous zirconia surface was functionalised through NH_3-temperature-programmed desorption (TPD) and liquid-phase Friedel-Crafts alkylation reactions. Functionalization of these self-assembled mesoporous nanoparticles into a strongly acidic nanostructured material has not been discovered. Compared to the mesoporous zirconia, synthesis of self-assembled zirconia nanoparticles surveyed by functionalization can offer an another way to yield functionalized mesoporous materials lively in acid catalytic reactions.

In some work, the reasonable inorganic material zirconium oxychloride and oxalic acid were castoff as raw materials to prepare mesoporous zirconia by a sol–gel method[8] with the support of PMMA as a template. Importantly, the space occupied by the PMMA particles analysts from the micron or submicron size range to the nanosized range as a result of the physical collapse that attends the illustration of zirconia.

It is known that dyestuff in wastewater from various industries such as textile, paper, leather, and plastics is difficult to remove[9], because it has disobedient molecules, is resistant to aerobic digestion, and is stable to oxidizing agents. Hence, the removal of dyestuff from waste effluents becomes environmentally important.



During textile processing, large numbers of chemically different dyes are directly appears in the form of wastewater and are directly discharged into surrounding environment, mostly into aquatic ecosystem nearby or on the land. It will pollute the drinking water and make the water unfit for other domestic purposes. Some physicochemical methods such as adsorption, precipitation, photo-oxidation, coagulation, flocculation, reduction, electrochemical treatment, photo degradation[10] have been used to remove the colour from wastewater. Recently, research focused on microbial biomass for the removal of fouling dyes[11] from the wastewater. Decolourization of dyes using microbes is an eco-friendly and cost effective processes. Several techniques are available for the treatment of the dyes such as Adsorption, photo-degradation, biodegradation, membrane separation, chemical coagulation and electrocoagulation are an electrochemical technique destroying the colour groups, a bio-degradation process mineralizing the colourless organic intermediates, chemical oxidation including homogeneous and heterogeneous photo catalytic oxidation. Dye removal by microorganisms takes place through three mechanisms; bio sorption, bioaccumulation, and biodegradation. Generally, adsorption process of the organic pollutants can affect their environmental behaviours such as transport, degradation, volatilization, bioaccumulation, subsequently, influence the final fate of the pollutants in the environment. Compared to filamentous fungi and yeast, bacteria have exhibited the attractive features, easy to manipulate, fast growth rate and high adaptive capacity. Bacteria are able to grow under

various extreme conditions of pH, temperature, nutrient availability and high pollutant concentrations, and can adapt in the natural environment. Among the many techniques of dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of dyes. Adsorption with activated carbon is time-consuming and costly. Photo-oxidation by ultraviolet (UV) rays in the presence of hydrogen peroxide (H_2O_2) or titanium dioxide (TiO_2) requires the use of additional chemicals

Methyl blue dyes are extensively used in textiles, printing, leather, cosmetics, rubber, plastics, paper and food industry. The release of these dyes into the environment is a major concern. These dyes are highly visible and undesirable even at very low concentration, and are recalcitrant molecules, mutagenic and toxic to mammalian cells. Improper disposal of dyes leads to reduction in sunlight penetration that causes decrease in photosynthetic activity. Therefore, it is very necessary to remove the wastewaters containing these dyes prior to discharge in to the environment. It is estimated that 1 to 15% of the dye is lost during dyeing and finishing processes due to the low dye fixation levels on the textile fibres. The disposal of coloured wastewater is a cause of major environmental concern since coloured effluent is undesirable not only from an aesthetic point of view, but it is also highly toxic. As a result, a significant amount of these dyes can exist in effluents from dyeing processes. Most synthetic dyes are toxic to human and aquatic life.

Aims and objectives

1. Synthesis of functionalised mesoporous zirconia.
2. To characterise the material by using instrumental techniques like XRD, SEM, FTIR and BET.
3. To remove methyl blue by using the material.
4. Optimization of the process with the variation of different process parameters.

Chapter-2

2. Materials and Methods

2.1. Materials

All chemicals used in this study were of AR grade and obtained from Merck (Germany). All glassware's used of borosil and tarson make. In all experiments, Millipore water was used for preparation, dilution and analytical purposes of the solutions. Stock solutions of the methyl blue were prepared by dissolving 1 mg of methyl blue (Merck) in 1 L of milipore water. Different concentrations of test solutions of methyl blue were prepared by proper dilution of the stock solutions.

Chemicals: Pluronic F127 (M_{av} =12600, $EO_{106}PO_{70}EO_{106}$) and zirconium (IV) butoxide [$Zr(OC_4H_9)_4$] were purchased from Sigma-Aldrich. Hydrochloric acid (HCl) citric acid (CA) and (3-Mercaptopropyl) trimethoxysilane (MPTMS) were obtained from Merck.

2.2. Material Preparation

2.2.1. Synthesis of mesoporous zirconia.

Synthesis: The synthesis of the material was carried out by the preparation of self-assembled mesoporous zirconia nanoparticles. In this synthesis, 20 mL absolute ethanol was acidified with 1.65 g (35 wt %) hydrochloric acid. Then 1 g pluronic F127 was added and was allowed to stir until it gets dissolved. After that dissolving 0.630 g (0.003 M) of citric acid was added to it under vigorous stirring. This mixture was stirred at room temperature for 2 h. After that, 3.84 g (0.01 M) zirconium (IV) butoxide taken in absolute ethanol was added slowly to the solution. The mixture was covered and was stirred at constant temperature at 343 K for 2 days to obtain the solid product. Calcination was carried out by slowly increasing the temperature to 773 K (1 K min^{-1} ramping rate) followed by heating at 773 K for 5 h in the presence of air to obtain template-free self-assembled mesoporous zirconia nanoparticles represented in Figure 1.

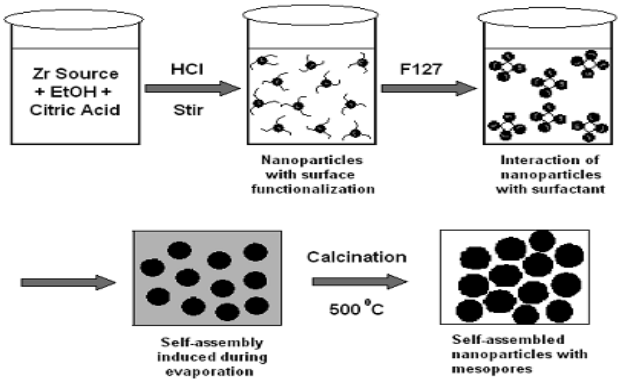


Figure 1. Mechanism for formation of self-assembled ZrO_2 nanoparticles with microscopic ordering through evaporation-induced self-assembly (EISA)

2.2.2. Synthesis of Thiol Functionalized mesoporous zirconia

Synthesis: The synthesis of thiol functionalized mesoporous zirconia. In this synthesis, 5 gm of mesoporous zirconia was pre-heated at 140 °C for 2 hours and then immersed into 50 ml of toluene and 10 ml of MPTMS in a 250 ml flask. The mixture was refluxed for 4 hours and the solid produced was filtered, washed with 100 ml ethanol and oven dried at 80 °C for 1 hour to produce a mercapto-functionalized (MP-MZ) respectively shown in Figure 2..

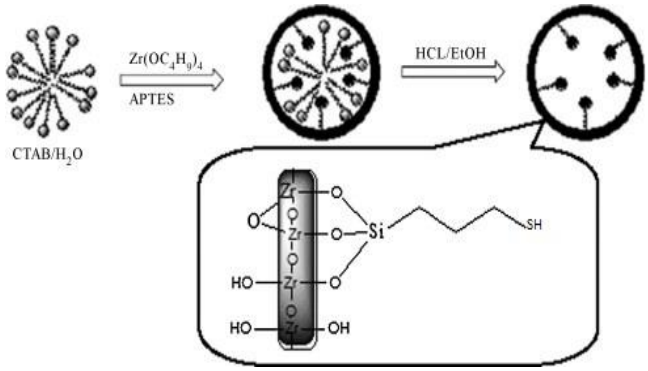


Figure 2. Synthesis of thiol functionalized mesoporous zirconia

2.3. Characterization of Adsorbent

The powder X-ray diffraction (XRD) of mesoporous zirconia was determined by using Philips X'Pert X-ray diffractometer with a Cu Kα radiation generated at 35 kV and 30 mA. Scattering angle 2θ was ranged from 10° to 80° at a scanning rate of 2 degree/minute and was analysed using standard software provided with the instrument. The surface micro-morphology of materials was investigated using scanning electron microscope (SEM)

operated at an accelerating voltage of 20 KeV, JOEL model JSM- 6480LV (Japan). The BET surface area was measured at liquid N_2 temperature using the Brunauer–Emmett–Teller (BET) surface area analyser (Quanta chrome AUTOSORB-1, USA). The samples were degassed at 150 °C in vacuum. Helium was used as carrier gas and surface area was measured by N_2 adsorption–desorption method. FT-IR spectra of the samples were obtained by using PerkinElmer FT-IR Spectrometer Spectrum RX-I. Calibration was made using proper concentration of standard solution prepared from stock solution by dilutions.

2.4. Batch Experiments

Adsorption of methyl blue on to thiol fictionalised mesoporous zirconia was studied at room temperature by batch adsorption method. A fixed amount of dry adsorbents 0.02 g was added to a series of capped volumetric poly lab plastic bottles containing 50 mL of 50 ppm methyl blue solution and shaken at 400 rpm using a temperature-controlled water bath with shaker. The bottles were capped tightly for all tests to avoid change in concentration, due to evaporation. The pH was adjusted to the desired level by adding required amounts of 0.1 M HCl or 0.1 M NaOH solutions. A number of experimental parameters such as adsorbent dose (0.01 g–0.09 g), contact time (15 min–75 min), initial concentration of adsorbate (25 mg/L–125 mg/L), pH (2–9) and temperature (27 °C) which affect the adsorption process have been studied to investigate the removal process. The solutions were stirred using magnetic stirrer at about 200 rpm for 1 hour. After stirring for a period of predetermined time, the solutions were allowed to settle for 10 min and wash the sample with distilled water. The samples were centrifuged at 6000 rpm for 20 min and filtered through Whatman 42 filter paper. The filtrate was used for the analysis of remaining methyl blue concentration in the solution.

3. Result and Discussion

3.1. Characterization of Adsorbent

The BET surface area and pore diameter was measured for mesoporous zirconia (MZ) and 5, 10, 15, 20 % Marcapto mesoporous zirconia (MPMZ) shown in Table 1. The XRD pattern of mesoporous zirconia and thiol functionalized mesoporous zirconia samples are shown in Figure 3. A single broad peak in their respective small-angle powder XRD patterns indicating long-range periodicity among the meso structures with some disorders. As evident from Figure 3 that with increase in percentage of thiol functionalised reagent the peak intensity decreases. The FTIR spectra of thiol functionalized mesoporous zirconia samples are shown in Figure 4. Bands around 3400 cm^{-1} and 1630 cm^{-1} stretching and bending vibration of water. 2550 cm^{-1}–2600 cm^{-1} peaks indicate the presence of S-H bond confirming thiol functionalization on mesoporous zirconia.

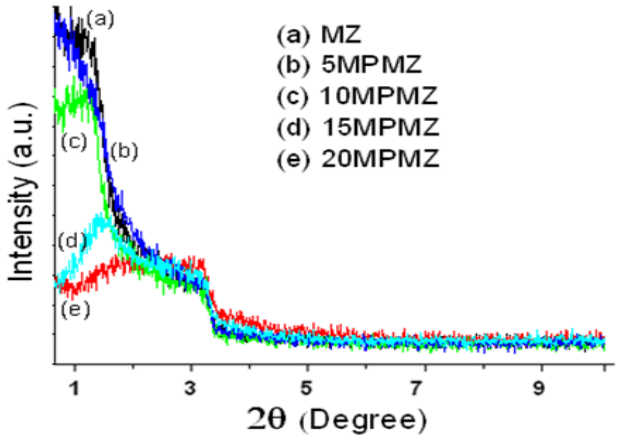


Figure 3. XRD of thiol functionalized mesoporous zirconia.

Table 1: Surface properties of thiol functionalizes mesoporous zirconia samples

Adsorbent	Surface area (m^2/g)	Avg. Pore diameter (nm)
MZ	136	4.34
5MPMZ	118	4.29
10MPMZ	102	4.27
15MPMZ	74	4.15
20MPMZ	55	4.01

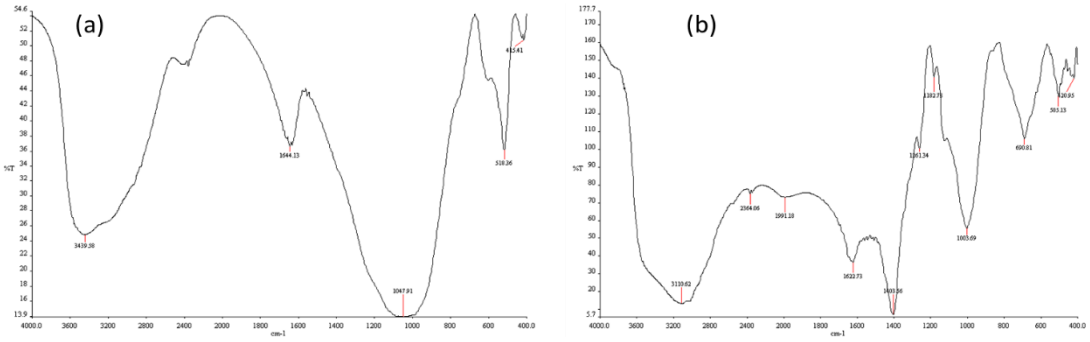


Figure 4. FTIR spectra of (a) mesoporous zirconia (b) thiol functionalized mesoporous zirconia

The SEM image of mesoporous zirconia clearly indicates the rounded shape aggregate particles (poorly crystallized/amorphous forms) due to the presence of some mineral phases mainly calcite and sodalite shown in Figure 5. These mineral phases are more soluble in an acidic environment. SEM images of thiol functionalized mesoporous zirconia clearly indicate the presence of shiny patches over the rounded shape aggregates confirmed the adsorption. These mesoporous materials have retained their respective meso structure during calcinations and thiol functionalization. SEM image of the 10% thiol functionalizes mesoporous zirconia shows uniform tiny spherical nanoparticle of thiol functionalizes mesoporous zirconia material.

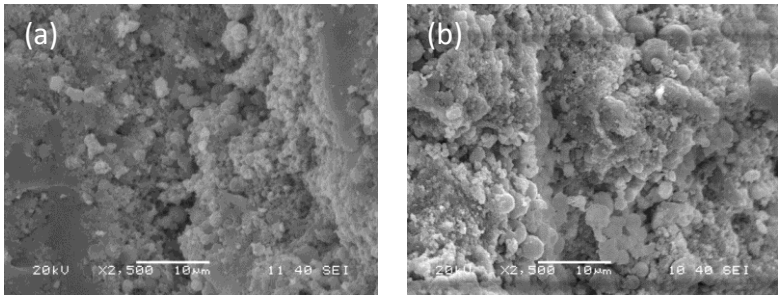


Figure 5. SEM image of (a) mesoporous zirconia (b) thiol functionalized mesoporous

3.2. Effect of adsorbent dose and pH

Adsorption of methyl blue at different adsorbent dose and pH was studied for initial methyl blue concentration of 10 mg/L to know the rate and equilibrium data. The results of the experiments are presented in Figure 6. The percentage removal of methyl blue was enhanced up to 60–100 % by increasing the adsorbent dosage to 0.01–0.03 g respectively, at room temperature and neutral pH. Because number of active sites increases with respect to increase of adsorbent dose. However, it was observed that after dose of 0.02 g, there was no significant change in percentage removal of methyl blue may be due to overlapping of active sites. Thus 0.02 g/50 mL was considered as optimum dose and was used for further study. The effect of pH on methyl blue adsorption on thiol functionalized mesoporous zirconia is summarized in Figure 7. The initial pH of the methyl blue solution was adjusted from 1 to 9 using 0.1M HCl or 0.1 M NaOH. The percentage removal of methyl blue by material is constant from 100% for increase in pH from 5 to 9, for initial lead concentration of 50 mg/L. The maximum percentage removal was found to 99.8 % at pH 5. After pH 5 there is no significant changes in percentage removal. This may be due to the fact that with increase in pH, OH^- concentration in the solution increases which makes partial dissolution of methyl blue in the aqueous solution.

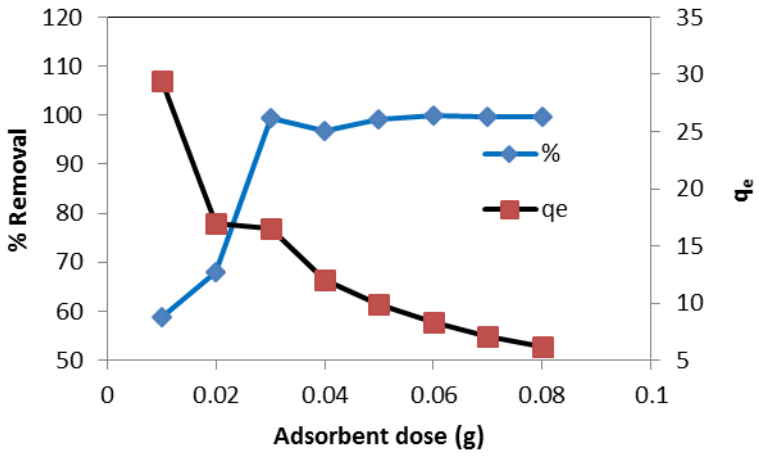


Figure 6. Adsorbent dose versus percentage removal of Methyl blue with initial concentration of 10 mg/L, temperature 27 °C and pH 7.

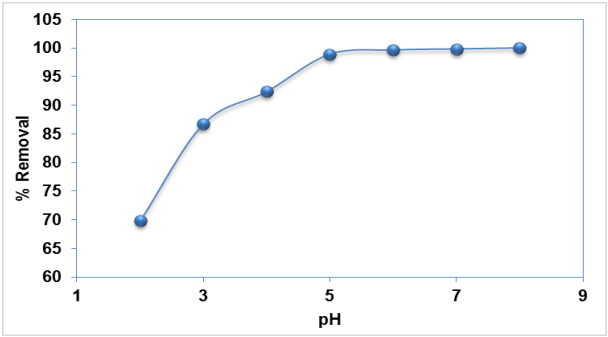


Figure 7. pH vs percentage removal of Methyl blue with initial concentration of 50 mg/L and adsorbent dose 0.02 mg/L, time 60 min.

3.3. Effect of contact time and adsorption kinetics

Adsorption of methyl blue at different contact times was studied keeping constant the methyl blue concentration (50 mg/L), adsorbent dose (0.02 mg/L) and pH 5 of the solution. The result is presented in **Figure 8**. The percentage removal was found to increase from 42.5% to 90% for a contact time of 15 min–90 min. It is clear from the figure that the methyl blue adsorption rate is high at the beginning of the adsorption, may be due to the adsorption sites are open and Methyl blue interact easily with these sites. A larger amount of methyl blue was removed in the first 60 min of contact time and methyl blue uptake becomes almost constant after 60 min, this indicates the possible monolayer formation of methyl blue on the outer surface and that can be considered as equilibrium time of methyl blue adsorption.

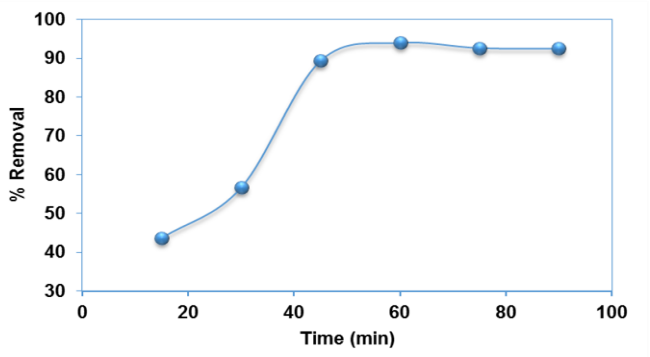


Figure 8. Time versus percentage removal of methyl blue with initial concentration of 50 mg/L, adsorbent dose 0.02 mg/L and pH of the solution 5.

The rate constant K_1 for the adsorption of methyl blue was studied by Lagergren rate equation for initial lead concentration of 50 mg/L. Pseudo-first-order rate expression of Lagergren equation:

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1 t}{2.303}\right) \quad (1)$$

where q_e and q_t are the amount of substance adsorbed (mg/g) at equilibrium and at time t (min), respectively. K_1 is the pseudo-first order rate constant (min^{-1}). The K_1 and correlation coefficient R^2 were calculated from the slope of the linear plot of $\log(q_e - q_t)$ versus 't' at different time intervals shown in Figure 9.

The pseudo-second-order rate expression is:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^{\,2}} + \frac{t}{q_e} \quad (2)$$

where K_2 is the pseudo-second-order rate constant ($g \cdot mg^{-1} \cdot min^{-1}$) and calculated from the slope and intercept of the plot t/q_t versus time 't' was almost linear shown in Figure 10.

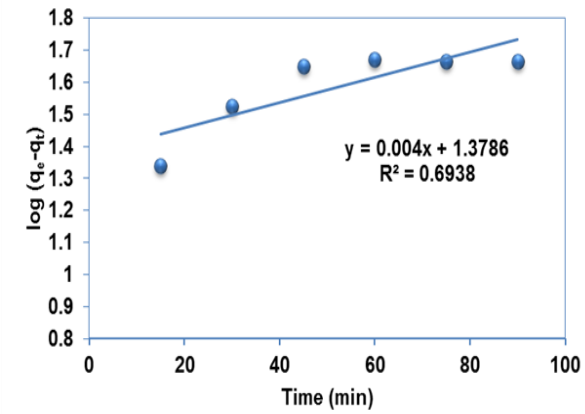


Figure 9. Pseudo-first-order kinetics Model

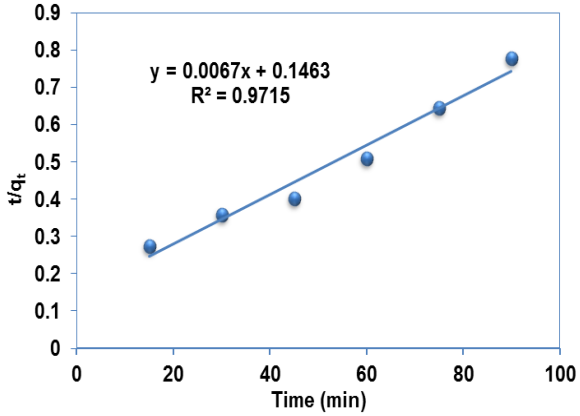


Figure 10. Pseudo-second-order kinetics Model

The K_1 and R^2 were found to be 0.0091 and 0.6938, respectively, in pseudo-first-order rate model and the values of K_2 and R^2 were found to be 0.0003 and 0.9715, respectively, given in **Table 2**. From the table it was observed that the low value of K_2 and high value of R^2 indicates that the adsorptions followed pseudo-second-order kinetics.

Table 2. Kinetics constants and related regression coefficients

Initial Methyl blue concentration (mg/L)	Pseudo-first-order Model			Pseudo-second-order Model		
	q_e (mg/g)	k_1	R^2	q_e (mg/g)	k_2	R^2
50	3.9692	0.0091	0.6938	150.2996	0.0003	0.9715

3.4. Effect of Temperature

The temperature has a noticeable effect on the adsorption capacity of the adsorbent. The effect of temperature prompting the adsorption has been studied in the range of 35–75 °C. The effect of temperature and the percentage removal of methyl blue with initial concentration of 50 mg/L are shown in **Figure 11**. It is observed that the percentage removal of methyl blue increases from 83% to 100% to with increasing temperature 35–65 °C which indicates the endothermic nature of the process and maximum adsorption at 100% obtained at 65 °C which is the equilibrium temperature of the solution. An increase in temperature involves an increased mobility of the metal ions and a decrease in the retarding forces acting on the diffusing ions. These result in the enhancement in the sorptive capacity of the adsorbent.

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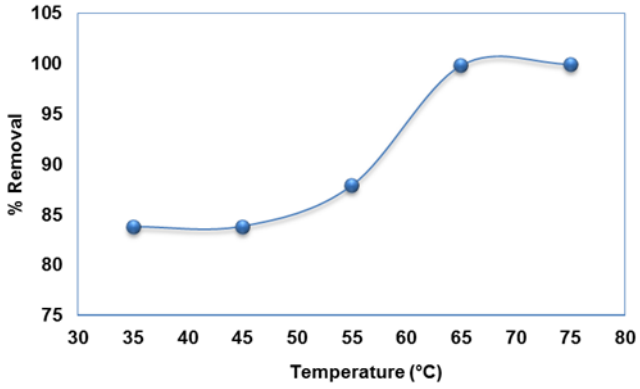

Figure 11. Temperature versus percentage removal of Methyl blue with initial concentration of 50 mg/L, adsorbent dose 0.02 mg/L, pH of the solution 5 and time 60 min.

3.5. Effect of Initial concentration and Adsorption isotherm

Batch experiments were performed to investigate the effect of initial methyl blue concentration from 25 mg/L to 125 mg/L with optimum adsorption dose on methyl blue

adsorption. When the initial concentration of methyl blue was 25 mg/L the removal percentage was 94% means the removal is 9.4 mg whereas, when the initial concentration was 125 mg/L the percentage removal was 51.9 % means the removal is only 5.1 mg out of 125 mg. Hence it is evident from the result that the percentage removal of methyl blue decreased from 94% to 51.9% with increasing initial concentration of 25 mg/L to 100 mg/L The reduction in methyl blue adsorption is due to the deficiency of available active sites required for the high initial concentration of methyl blue. The higher uptake of Methyl blue at low concentration may be attributed to the accessibility of more active sites on the surface of the adsorbent for smaller number of adsorbate species.

Common adsorption isotherm has been used to evaluate the adsorption capacity of an adsorbent for an adsorbate. The linearized Langmuir adsorption isotherm equation which is effective for monolayer sorption on a surface by finite number of equal sites is as follows:

$$\frac{C_e}{q_e} = \frac{1}{(q_m b)} + \frac{C_e}{q_m} \qquad (3)$$

where C_e is the equilibrium concentration of adsorbate in solution (mg/L), q_e is the amount adsorbate adsorbed at equilibrium (mg/g), q_m is the theoretical maximum adsorption capacity (mg/g) and b is the Langmuir constant (L/mg). The linear plot of $1/C_e$ versus $1/q_e$ with correlation coefficient R^2=0.9926 indicates the applicability of Langmuir adsorption isotherm shown in Figure 12**.** This indicates a monolayer sorption of methyl blue onto the adsorbent surface. The maximum adsorption capacity (q_m) and binding energy constant (b) of thiol functionalised zirconia for methyl blue was 183.7142 mg/g and 0.2686 L/mg, respectively according to Langmuir model.

Freundlich adsorption isotherm adopts multilayer adsorption on heterogeneous surfaces. Linearized form of the Freundlich equation is given by the following equation:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (4)$$

where q_e is the amount of methyl blue adsorbed at equilibrium time (mg/g), C_e is the equilibrium concentration of methyl blue in the solution (mg/L), K_f is the adsorption capacity (mg/g) and n is an empirical parameter. The value of K_f, n and R^2 are found to be 5.4022 mg/g, 2.7718 and 0.8917, respectively, shown in Figure 13.

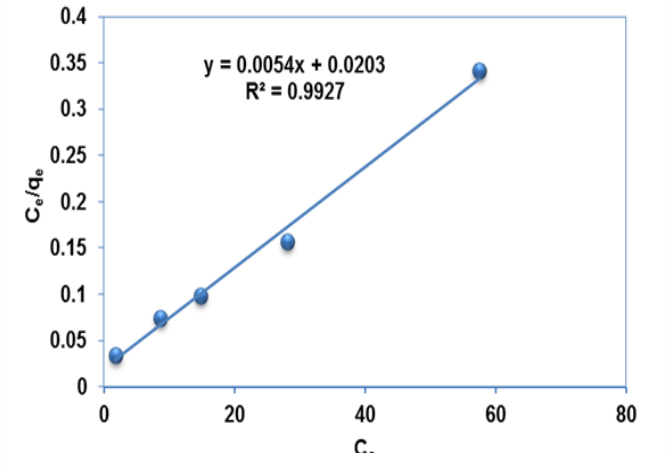

Figure 12. Langmuir adsorption isotherm plot of C_e/q_e Vs. C_e

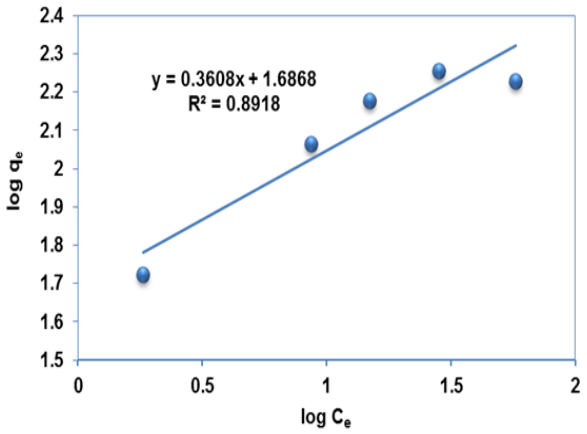

Figure 13. Freundlich adsorption isotherm plot of log q_e Vs. log C_e

The value of Langmuir and Fruendlich parameter constant was summerized in Table 3. From the Table 3 it was observed that higher correlation coefficient of Langmuir isotherm indicates that the adsorption data fits better with Langmuir model then Freundlich model.

Table 2. Langmuir isotherm and Freundlich isotherm model data

Parameters / Model	Langmuir isotherm	Freundlich isotherm
q_m (mg/g)	183.7142	
b (L/mg)	0.2686	
R^2	0.9926	
K_f		5.4022
1/n		0.3607
R^2		0.8917

Chapter-4

4. Conclusion

The present work shows that the thiol functionalized mesoporous zirconia can be used as adsorbent for the removal of methyl blue from aqueous solutions successfully. The material has not only a high adsorption capacity for the methyl blue but also capable of lowering the concentration to a great extent. The concentration gradient is a fundamental force that transfers the ion from solution to adsorbent surface and diffuses ion into the inside of adsorbent. The adsorption kinetics was found to follow pseudo-second-order rate equation and equilibrates within 60 min. The adsorption isotherm is better described by the Langmuir isotherms. The maximum adsorption capacity of material was 183.7142 mg/g. The adsorption of methyl blue by materials.

Future Work

1. To take up the dissorption of the material by suitable reagent for its reuse.
2. To make column study for its practical application.
3. To establish the mechanism of the process.
4. The detail characterization of the material synthesized.

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