

PREPARATION OF MAGNETIC/SILICA/QUARTERNARY-CHITOSAN BY SOL-GEL METHOD AND ITS STABILITY IN VARIOUS pH MEDIUM

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ABSTRACT

This research aimed to study SiO₂/quaternary-chitosan-coated magnetic material synthesis using the sol-gel method through two synthetic routes. The step of Route 1 was the methylation of the amine group on chitosan using methyl iodide and sodium hydroxide with dimethylformamide : water (1:1) as a solvent at room temperature for 48 hours to produce trimethyl chitosan. The next step was the sol-gel reaction. The magnetic was coated with silica and then added to the trimethyl chitosan solution that has reacted with (3-glycidyloxypropyl)trimethoxysilane as a crosslinker. Whereas Route 2 was the opposite of route 1, magnetic coating with chitosan silica was carried out first through the sol-gel reaction, followed by the methylation reaction. The synthesis results were characterized by their functional group, structure, crystal size, magnetic properties, and morphology. The Fe₃O₄/SiO₂/quaternary-chitosan material was successfully synthesized, as indicated by the increase in the specific absorption band for C-H methyl and the decrease in the N-H amine absorption. Route 1 produced material with more quaternary ammonium groups and porous surface but inhomogeneous, while Route 2 produced thicker magnetic coatings. Both materials had stability in the range of pH 3-6 so that they could be applied as adsorbents for anionic compounds in this range.

Keywords: Magnetite, Silica, Chitosan, Trimethyl Chitosan, Sol-gel, Coating

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INTRODUCTION

Nowadays, besides cationic metals, anionic pollutants are also of particular concern where these anionic pollutants enter the water supply through various works as well as mining, ores refinement, fertilizer, batteries, tanneries, pulp, and paper industries, etc.¹⁻² Some of these anions occur naturally in nature, such as nitrates and nitrites in mineral deposits, fluorine in rocks, and cyanide compounds in plants and animals.³ The anionic species include nitrate, nitrite, chloride, sulfide, fluoride, and cyanide, while metal anion complexes such as chromate, arsenate, selenate, and aurate. These anionic species become harmful to the environment if they occur in high concentrations.

Several industrial activities produce anionic waste containing precious metals that are feasible for recovery. For example, gold and silver cyanide are found in industrial waste in gold and silver mining, electroplating, printed circuit board industries, and jewelry units.⁴ Platinum and palladium are also precious metals that have to be recovered potentially from catalytic converters, carbon-based catalysts, electronics waste, and jewelry.⁵⁻⁶ Adsorption is a promising method for the removal of anionic pollutants or recovery of precious metals because of its low cost, simplicity, and high efficiency, especially at low concentrations where the adsorbent is created specifically for certain targets.⁷⁻⁸ The development of adsorbents with high performance is then challenging.

The development of adsorbents with magnetic characters today has attracted the researcher's consideration regarding their properties, which can have a significant effect in accelerating separation and increasing efficiency in water treatment⁹ as well as ease of separation by utilizing external magnetic fields.¹⁰ Among the magnetic materials, magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃) are the most studied owing to their

small size and large surface area, allowing a high adsorption capacity of analytes.¹¹ However, magnetite has disadvantages where it is easily oxidized, causing loss of magnetic properties and agglomeration and decreasing the active group.¹²⁻¹³ Therefore, an inert coating is needed to protect the magnetite core, such as silica gel, with good mechanical, chemical, and thermal stability.^{11,14}

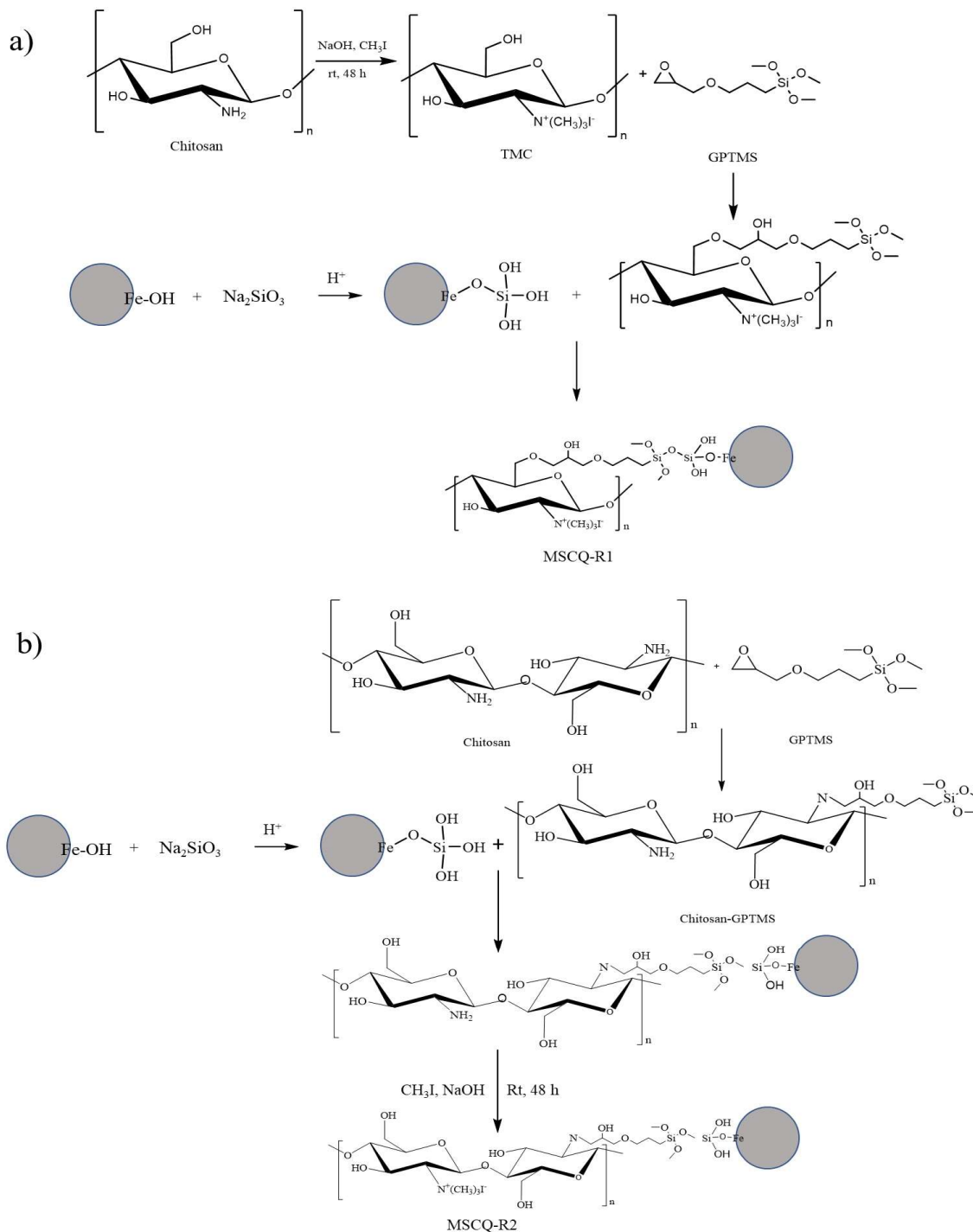


Fig-1: Reaction Mechanism Model of (a) Route 1, (b) Route 2^{15,16}

Modifying the silica surface is required to achieve selectively anionic adsorption through positively charged groups. By doing so, the adsorption mechanism can be effective on a broader pH range. One of the materials that meet the criteria is quaternary chitosan, which has a permanent positive charge. Magnetic

quaternary chitosan hybrid nanoparticles have been successfully synthesized using glycidyltrimethylammonium chloride and applied to uptake diclofenac from water.¹⁷

The amine group in chitosan can also be derivatized into quaternary ammonium through a methylation reaction using methyl iodide as a reagent and NaOH as a base to produce trimethyl chitosan.¹⁶ On the other hand, the functionalization of chitosan on silica coated-magnetite requires a crosslinker such as glycidyloxypropyltrimethoxysilane (GPTMS) through the opening of the epoxide ring by the amine group of chitosan.¹⁸ So, this research aimed to synthesize MSCQ through two routes to find out which route can generate more quaternary ammonium groups. Route 1 was carried out by converting the amine group in chitosan into quaternary ammonium, then followed by a sol-gel reaction between magnetic-silica and quaternary chitosan using GPTMS as a crosslinker. This route directed the epoxide ring-opening of GPTMS by the hydroxyl group of chitosan¹⁹ and resulted in the material being named MSCQ-R1. While route 2 was the opposite of route 1 where the sol-gel reaction was carried out first, followed by a methylation reaction and produced material MSCQ-R2. The purpose of this research was to produce an adsorbent material with a quaternary ammonium group which was amorphous and stable at pH 3-6. So, the synthetic materials were evaluated for their functional group, crystal structure, morphology, magnetic properties, and stability in various pHs.

EXPERIMENTAL

Preparation of Iron Sand

Iron sand collected from Kulonprogo, Yogyakarta, was dried in the sun, then the magnetic material was separated by a neodymium magnet, washed with distilled water, and dried at 90 °C. The dried magnetic material was sieved 200 mesh after being crushed manually.

Synthesis of MSCQ-R1

Firstly, the number of amine groups in chitosan was determined by volumetry.¹⁵ A total of 0.5 g (3 mmol) chitosan was dissolved in DMF (Merck; 99.8%): water (1:1) 30 mL and then added 18 mL NaOH (Merck; >99%) 0.5 M (9 mmol). This solution was then added 18 mmol of methyl iodide (Merck; 99%), and the reaction was conducted for 48 hours at room temperature. This methylation reaction was repeated four times, and the reaction product was precipitated with 200 mL ethanol (99.9%) overnight and separated by centrifugation.¹⁶ Trimethyl chitosan (TMC) obtained from the methylation reaction was dissolved in 30 mL DMF: water (1: 1), stirred for 2 hours then allowed to stand overnight. A total of 0.67 mL GPTMS (Sigma-Aldrich; ≥98%) (3 mmol) was added to the chitosan (Sigma-Aldrich; ≥75% deacetylated) solution (1% w/t in 1% acetic acid) and stirred for 1 hour. In another flask, 0.5 g of magnetic material was acidified with 1 mL HCl (Merck; 37%) 1 M and then was added 1 mL of sodium silicate (Sigma-Aldrich; ~26.5% SiO₂) (3 mmol) and 1 mL of distilled water. The mixture was stirred while adding 1 M HCl drop per drop until it reached pH 10²⁰, then immediately poured into the TMC-GPTMS solution and stirred for 1 hour at room temperature until it was homogeneous. After homogeneous NH₄OH (Merck; 25%), 0.5 M was added dropwise until pH 7, and the mixture became a gel. The formed gel was allowed to stand for 24 hours, then dried at 60 °C and washed with distilled water. The mechanism reaction model is shown in Fig.-1.

Synthesis of MSCQ-R2

The synthesis was carried out in the same way as Route 1 but in a different order where the reaction of the silica-chitosan coating on the magnetic material by the sol-gel method was carried out first, then followed by methylation of the amino group of chitosan. The synthesized material was then characterized to determine changes in functional groups (FTIR spectrometer, Bruker-Tensor II), structure and size crystal (X-Ray Diffractometer, Bruker D2 Phaser), morphology (Scanning Electron Microscope, Phenom Desktop ProXL, and Transmission Electron Microscope, Hitachi HT 7700), and magnetic properties (Vibrating Sample Magnetometer, Oxford 1.2H).

Stability of MSCQ in various pH

A total of 10 mg of material was added with 15 mL of water (pH 1-8) and then was stirred for 2 hours. The filtrate was separated by an external magnet, and then chitosan leached was determined with a UV-Vis spectrophotometer at 197.5 nm (as the maximum wavelength of pure chitosan solution).

RESULTS AND DISCUSSION

Functional Group

The success of the synthesis of MSCQ via two routes was determined by various instruments. The first characterization was carried out to determine the change in the functional groups using FTIR, which is shown in Fig.-2. Chitosan has several characteristic bands, namely at 3423 nm^{-1} which is the absorption band of O-H and N-H stretching vibrations, and the absorption band at 2881 nm^{-1} corresponds to C-H stretching vibration. The characteristic absorption bands of chitosan are shown at 1651 and 1573 nm^{-1} which are bands of C=O stretching and N-H bending.¹⁷ The absorption bands at 1419 and 1377 nm^{-1} show the vibrations of CH_2 bending and CH_3 symmetrical deformation of acetyl groups.²¹ The absorption bands at 1151 nm^{-1} and 1080 nm^{-1} refer to the asymmetric absorption of the C-O-C bridge and C-O stretching, respectively.

The presence of quaternary groups on MSCQ-R1 and MSCQ-R2 is indicated by the existence of bands at 1462 , and 1465 nm^{-1} , respectively, which is a typical absorption of asymmetric C-H stretching on N-CH_3 .²²⁻²³ Evidence that amines were successfully converted to a quaternary group is also shown in the sharpening of the absorption band at $2870\text{-}2930\text{ nm}^{-1}$ which is related to the symmetric and asymmetric C-H bond of the methyl group²⁴ where MSCQ-R1 absorption is sharper than MSCQ-R2. The decreased absorption intensity of N-H bending at around 1573 can also be used to confirm the formation of quaternary ammonium groups where there is no visible absorption in the area for MSCQ-R1 while in MSCQ-R2 the absorption is still visible but shifted to 1556 . The quaternarization level of MSCQ-R1 is higher than MSCQ-R2 due to several amines that have been used first to bind to GPTMS as a crosslinker. The remaining unconverted amine groups are in consequence of the less optimal methylation reaction for those bulky materials.

The coating silica on magnetite was confirmed through absorption bands at 1080 and 1068 nm^{-1} for MSCQ-R1 and MSCQ-R2, respectively, owing to Si-O-Si asymmetric stretching vibrations and supported by absorption at 796 and 785 nm^{-1} indicating the presence of Si-O symmetry stretching vibration. The Fe-O bond is shown from the absorption band around 545 nm^{-1} .²⁰⁻²⁵ Meanwhile, the absorption band in the area $943\text{-}950$ shows a Si-O-metal bond, and the bands at 451 and 447 correspond to Si-O rocking vibration²⁶. The MSCQ-R1 absorption band in this area is sharper, indicating that the material is less homogeneous than MSCQ-R2.

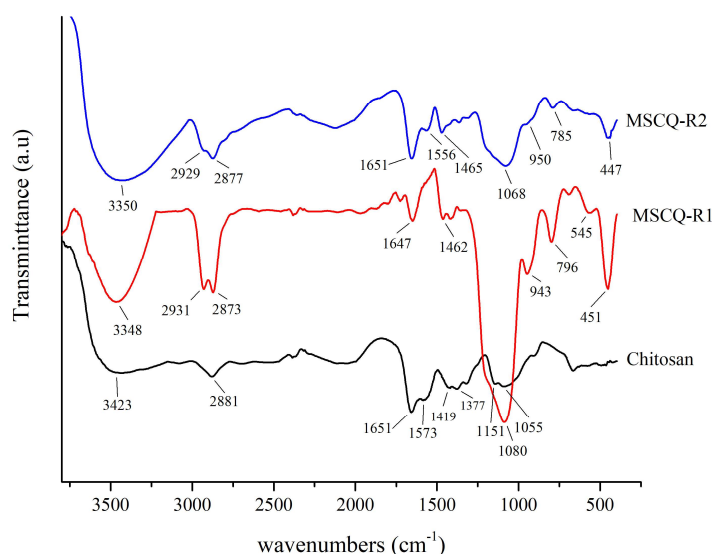


Fig.-2: FTIR Spectra of Material Synthesized

Structural Characterization

The synthesized material was characterized by XRD to determine the diffraction pattern shown in Fig.-3. There is no significant change in the diffraction pattern between the magnetic materials coated with silica quaternary chitosan through route 1 (MSCQ-R1), route 2 (MSC-R2), and silica-coated magnetic material

(MS). However, there is a decrease in the intensity of several peaks, especially at 2θ 30° due to the presence of silica chitosan coating on magnetite material.¹⁵ Besides, the amorphous phase of SiO_2 was also seen as broadband at 2θ 20 - 26° .²⁷ Chitosan does not contribute to the appearance of XRD peaks because chitosan does not have a crystalline structure.²⁸ The d_{311} crystal structure parameters and crystal size are shown in Table-1, which can be concluded that the crystal size increases after coating with quaternary chitosan silica and GPTMS as crosslinkers. The presence of GPTMS affected the crystal size, where to some extent, the higher amount of GPTMS, the larger the crystal size.²⁹ Meanwhile, when compared between the two synthesis routes, chitosan silica coating through route 2 resulted in a larger crystal size than route 1. The binding of GPTMS as a crosslinker through the hydroxyl group in the TMC (Fig.-1) was not optimal due to its low nucleophilicity than the amine group. This prediction is also supported by an indication of its low rendement. Crystal size can also be an indication of the adsorption performance, where the smaller the crystal size will increase the capacity and rate of adsorption.³⁰

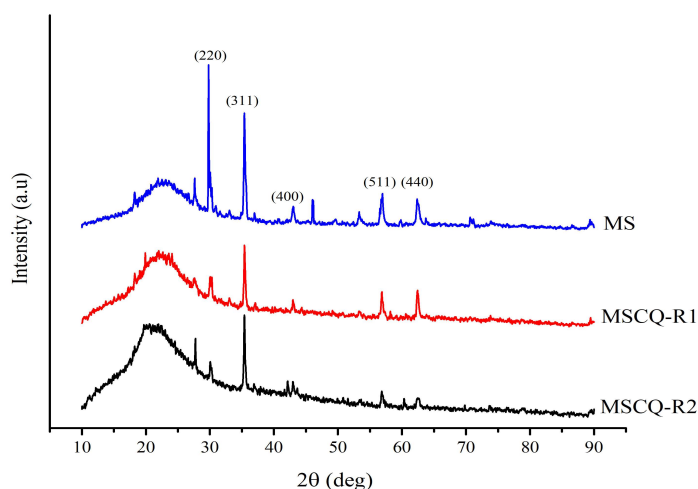


Fig.-3: XRD Pattern of Material Synthesized

Table-1: Structural Properties of Magnetic Coated with Silica/quaternary-chitosan

Material	2θ	d_{311} (nm)	D (nm)
MS	35.419	2.53	25.59
MSCQ-R1	35.425	2.53	28.23
MSCQ-R2	35.400	2.53	30.76

Morphology and Elemental Analysis

The morphology of the surface material was evaluated by the SEM image shown in Fig.-4. Route 1 produced material MSCQ-R1 coarser and more porous than Route 2. From the TEM image in Fig.-5, it can be observed that the synthesized materials have an irregular shape with the dark area representing magnetic material.³¹ However, this form cannot be clearly identified because there is still aggregation, so the coating did not significantly prevent aggregation, and the particle size can't be determined.³² Elemental analysis of both materials using EDX is shown in Table-2. The success of quaternary chitosan coating on magnetic/silica is indicated by the presence of C, N, and I atoms, where the percentages of C and N in MSCQ-R2 are higher than MSCQ-R1. So, it can be concluded that the chitosan coating on MSCQ-R2 is thicker than MSCQ-R1, which is in accordance with XRD data. However, the percentage ratio of iodine to nitrogen for MSCQ-R1 is higher than MSCQ-R2, which indicates a higher quaternary ammonium group.

Table-2: Elemental Analysis of Synthetic Materials by EDX

Material	% Atoms							
	O	C	Si	N	I	Fe	Al	Ti
MSCQ-R1	49,00	34,85	11,44	3,81	0,42	0,31	0,13	0,04
MSCQ-R2	41,35	41,17	6,97	8,84	0,42	1,02	0,11	0,12

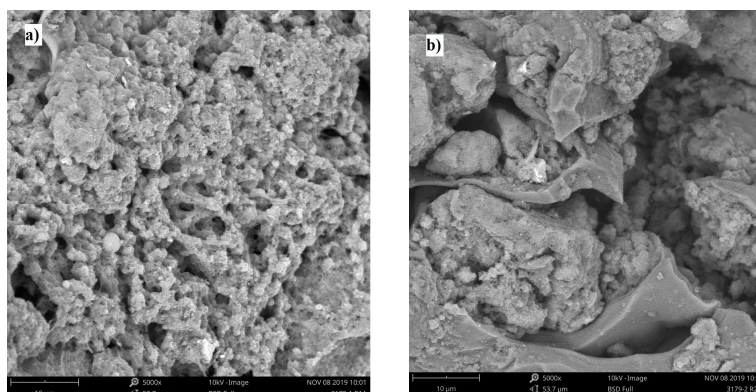


Fig.-4: SEM Images of (a) MSCQ-R1 and (b) MSCQ-R2

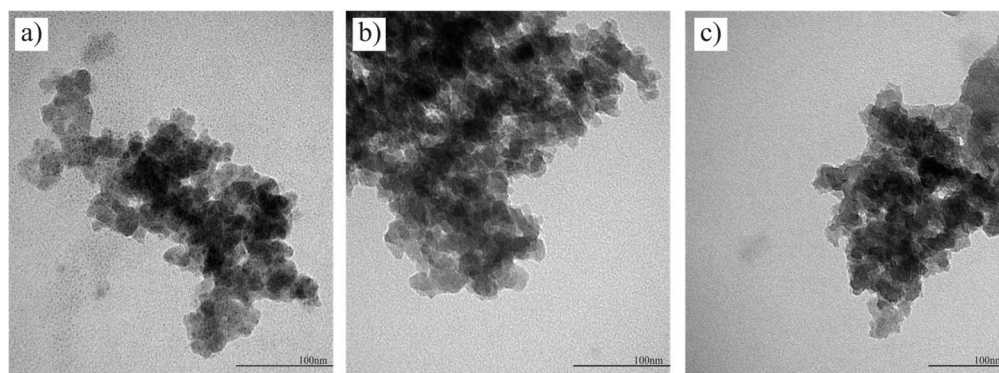


Fig.-5: TEM Image of Material (a) MS, (b) MSCQ-R1, and (c) MSCQ-R2

Magnetic Properties

The magnetic parameters of the synthesis results were determined using the VSM instrument by evaluating the hysteresis curve as shown in Fig.-6. All material from synthesis tends to have superparamagnetic properties characterized by the H_c value that is close to zero (narrow hysteresis curve), which values are shown in Table-3.³³ These materials are also classified as a soft magnet, which is prone to magnetization and demagnetization.³⁴ The magnetic saturation value of MSCQ-R2 is lower than MSCQ-R1, indicating that the silica chitosan coating is thicker³⁵, which is consistent with XRD data where the crystal size of MSCQ-R2 is larger than MSCQ-R1.

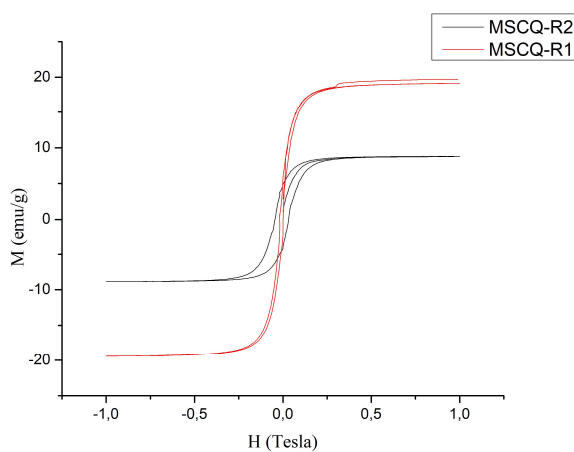


Fig.-6: Magnetization Curve of MSCQ-R1 and MSCQ-R2

Table-3: Magnetic Properties of Material synthesized

Material	Ms (emu/g)	Mr (emu/g)	Hc (10^{-2}) (Tesla)
MSCQ-R1	19.11	5.49	1.87
MSCQ-R2	8.76	2.14	1.99

Stability in Various pH

The stability evaluation of materials was carried out in the range of pH 1-8 to assign its stability at various pHs. Fig.-7 shows chitosan dissolved in the solution as measured by a UV-Vis Spectrophotometer at 197.5 nm where all materials tend to be stable at pH 3-6. Meanwhile, when viewed from the acidic pH, MSCQ-R1 has lower absorbance than MSCQ-R2 or magnetic/silica/chitosan (MSC). This may be due to the thinner layer of chitosan on MSCQ-R1 so that there was less dissolved in an acidic medium.

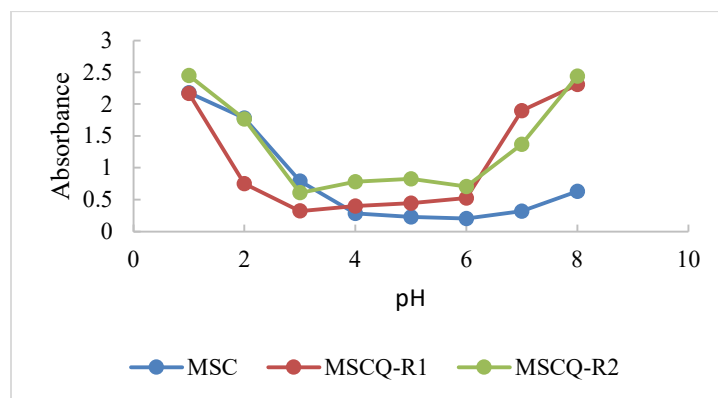


Fig.-7: The Absorbance of Chitosan leaching in Various pHs

However, at high pH MSCQ-R1 has the lowest stability. The change in the amine group to quaternary ammonium causes the material to dissolve more easily in water because the quaternary ammonium group is a hydrophilic group that increases the strength of charge and weakens the intermolecular hydrogen bonds, thereby increasing their solubility in water.³⁶⁻³⁷ Thus, MSCQ is more suitable for anionic adsorbents in the pH range 3-6.

CONCLUSION

Material magnetic/silica/quaternary-chitosan was successfully synthesized by Route 1 and Route 2. Based on FTIR spectra, MSCQ-R1 has more quaternary groups than MSCQ-R2 but tends to be inhomogeneous. The XRD data showed that silica/quaternary-chitosan coating did not affect the crystallinity of the synthesized material, where the crystal size of MSCQ-R2 was greater than MSCQ-R1. Either MSCQ-R1 or MSCQ-R2 has an irregular shape where the magnetic coating with silica/quaternary-chitosan did not significantly prevent aggregation between particles. The magnetic saturation value of MSCQ-R2 was lower than MSCQ-R1, indicating that the synthesis process with Route 2 provides a thicker coating than Route 1. The material has the prospect of being an adsorbent for anionic species in the pH range 3-6 due to its stability in this pH range.

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