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Rauf Yu. Aliyarov

Scientific Research Institute of Geotechnological Problems of Oil, Gas and Chemistry, ASOIU, Dilara Aliyeva Str.227, Baku, AZ 1010 Azerbaijan

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Phone: +994 12 4937957

E-mail: info@gpogc.az

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Novel adsorbents on the bases of functionalized chitosan and magnetite nanoparticles for removal of organic pollutants and heavy metal ions from water

Z.O. Gakhramanova[b], S. A. Mammadhanova[a] , S. S. Hasanova[a,b] ,N. S. Bayramova[b].

[a] Azerbaijan State Oil and Industry University, 20 Azadlig Ave., Baku, AZ1010, Azerbaijan

[b] Scientific Research Institute of " Geotechnological Problems of Oil, Gas and Chemistry", ASOIU, 20 Azadlig Ave., Baku, AZ 1010 Azerbaijan

Abstract
This paper reports about the successful functionalization of low molecular weight chitosan with 2,2-(ethane-1,2-diylbis(oxy))dibenzaldehyde and further conjugation of obtained gel with Fe_3O_4 nanoparticles. The functionalization of chitosan with dialdehyde occur through condensation reaction of chitosan amino group with carbonyl groups of dialdehyde that brings to the imine linkage that tithing the chitosan chains. The structure of prepared gel have been proved by NMR and FTIR spectroscopies. The morphology and composition of prepared conjugated gel@Fe_3O_4 have been studied by XRD and TEM analysis methods.
Keywords: Chitosan, 2,2-(ethane-1,2-diylbis(oxy))dibenzaldehyde, adsorption, Fe04, nanostructure, gel.
Corresponding author. Tel. 0555503579
Email address sibel.aliyeva2002@gmail.com

1. Introduction

The development of oil and petrochemical industry moving to the next level however exerts serious influence on the environment, pollution of water basins and greenhouse effect. One of the global problems at the moment is the leakage of oil and oil products leading to serious environmental problems. Enterprises aimed at oil transportation and oil and gas complexes are the most frequent water polluters [1]. As a result of poisoning by organic compounds and heavy metals, abiotic components including marine life and plants are killed, leading to the destruction of the ecosystem [2].
Currently, various methods of water purification have been developed and successfully applied. Among them there are such methods as: gravity sedimentation [3] and corrugated plate interceptors

[4],chemical pretreatment (coagulation-flocculation)[5], centrifugal separation using hydrocyclone [6], gas flotation [7,8] and dissolved gas flotation. Recently, biological water treatment processes using membrane bioreactor [9,10] as well as biotechnological water treatment methods have received much attention. One of the simplest and most effective methods of water purification is filtration using various porous materials such as ion-exchange polymers, resins, sand, clay, silica [11] ultrafiltration [12,13]; nanofiltration [14] and reverse osmosis [15,16]

The development and application of new materials as adsorbents is an urgent task in view of the increasing problems of ecological character, the use of biodegradable and biocompatible materials is very much in demand. Recently, there have been many reports in the literature that chitosan and its derivatives can be successfully used as adsorbents for the purification of polluted water [17].

Another promising material as adsorbents are nanomaterials. Recent advances in nanotechnology also present nanomaterials as effective adsorbents for the treatment of polluted water. The recent studies reported about advances of magnetite nanoparticles and nanocomposites applications in water remediation from organic pollutants [18].

Taking in consideration above mentioned we carried out the synthesis and characterization of chitosan derivatives on the bases of chitosan and dialdehyde with further conjugation with Fe3O4 nanoparticles [19,20].

2. Experimental part

Reagent and materials

Chitosan (Mol wt=50,000 Da), salicylaldehyde, 1,2-dibromethane, were obtained from Sigma-Aldrich, acetic acid(100%), ethanol(95%), (DMSO-d6, d, ppm), CTAB, K_2CO_3, distillated water, $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, NH_4OH(10%) were purchased from Merck.

Synthesis

Synthesis of 2,20-(ethane-1,2-diylbis(oxy))dibenzaldehyde.

The process stared with dissolving of 38.3 moles salicylaldehyde in 20 mL of DMSO followed by the addition of 37.7 moles of K_2CO_3. Then after the addition of 1.2-dibromoethane, we heated on a water bath for 3 hours followed by cooling for 3 hours with ice. After the time is over, it should be filtered, washed with distilled water and dried at ambient

Synthesis of gel on the base of chitosan and dialdehyde

In a round bottom flask we put 0.0016 mmol of chitosan and add 50 ml of acidified water. After 3 hours of stirring, at the temperature of 40℃ , added a solution of 0.18 mmol of dialdehyde in 10 mL of ethanol. The reaction was continued for 3 hours at constant stirring. Prepared gel was analyzed by FTIR, XRD and TEM methods.

Synthesis of magnetic nanoparticles

The process was performed in molar ratio of Fe^3 :Fe^{2+} as 2:1. In a round bottom flask we dissolved 27 mmol of $FeCl_3 \cdot 6H_2O$ in 50 mL distillated water followed by addition 13.4 mmol of $FeCl_2 \cdot 4H_2O$. The reaction was carried out in the nitrogen atmosphere and continued by stirring and heated to 60°C. After a 3 hours, we added 50 ml of NH_4OH 10% and stirred until the color of the solution turned black and pH of solution 9. Then 0.002 mmol of CTAB in 10 ml of distillated water added to the solution of formed magnetic nanoparticles for stabilization. After stirring we filtered and dried stabilized magnetic nanoparticles at the temperature of 70℃ for 2 hours.

Synthesis of gel@Fe3O4 nanoparticle

The 0.8 g of magnetic nanoparticles in 50 ml deionized water was exposed to an ultrasonic bath for 30 min. Then the sonicated mixture of magnetic nanoparticles slowly was added to the 60 ml of gel , with further stirring at 40 °C for 60 min.

3.Characterization

FTIR spectroscopy

The synthesized structure of chitosan derivative and gel@Fe3O4 nanoparticles have been analyzed by FTIR spectroscopy method. The spectra have been recorded FTIR spectrophotometer Thermo^{TM} Scientific^{TM} Nicolett iS20, using an attenuated total reflectance (ATR) accessory intherangeof4000–450cm1.

NMR spectroscopy

The NMR experiments were performed on a BRUKER FTNMR spectrometer AVANCE 300 (Bruker, Karlsruhe, Germany) (300MHz for ^{1}H and 75 MHz for ^{13}C) with a BVT 3200 variable temperature unit in 5 mm sample tubes using Bruker Standard software (Top Spin 3.1). Chemical shifts were given in ppm (d) and were referenced to internal tetramethylsilane (TMS). Multiplicities are declared as follows: s (singlet), d (doublet), t (triplet), q (quadruplet), and m (multiplet). Coupling constants J are given in Hz. The experimental parameters for ^{1}H are as follows: digital resolution=0.23Hz, SWH=7530Hz, TD=32K, SI= 16K,901pulse-length=10ms, PL1=3dB, ns=4, ds=2, d1=1s and for ^{13}C as follows: digital resolution=0.27Hz, SWH= 17985Hz, TD=64K, SI=32K,901pulse-length=9ms, PL1= 1.5dB, ns=1000, ds=2, d1=3s. The NMR-grade DMSO-d6 (99.7%, containing 0.3% H2O) was used for the solutions of synthesized compounds.

Transmission electron microscopy (TEM).

The TEM analysis of the nanostructures gel and gel@Fe_3O_4 was performed on a TEM JEOL-1400 (Japan) at 80–120kV. The ultrasonicated solution of gel in ethanol was placed on a carbon-coated grid and dried at ambient conditions.

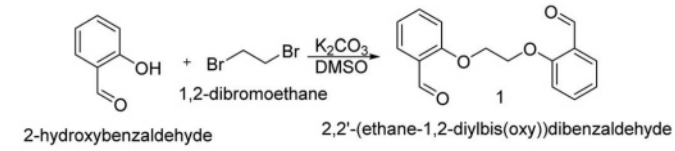
X-Ray powder diffraction analysis (PXRD).

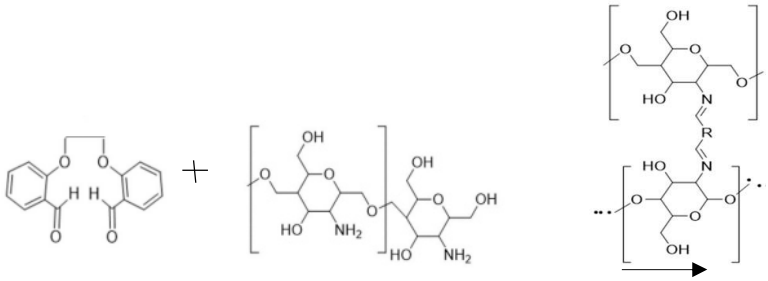
XRD analysis was performed under ambient conditions on a Rigaku Mini Flex 600 XRD diffractometer, equipped with Cu Ka radiation, to study the crystalline structure of the synthesized Fe3O4 nanoparticles and gel@Fe3O4. The samples were scanned in the Bragg angle range of 10^0–80^0 at 2 θ, 15 mA. The Williamson-Hallmethod was used to calculate the crystallite size.

7. Results and discussion

One of the promising materials is chitosan obtained by hydrolytic deacetylation of natural chitin, which is a structural component of the skeletons of all crustaceans and insectivores. Due to the presence of amine and hydroxyl groups in the macromolecule of chitosan such adsorption properties of binding heavy metal ions, organic pollutants and antimicrobial, but also being a natural polysaccharide it shows such properties as biocompatibility and biodegradability. Chitosan and its modifications are already being used for water purification. It is chemically modified in a variety of ways, including coupling with other polymers or inorganic materials, complexation and crosslinking to reduce its solubility in acidic media and to increase its chemical stability and flexibility. The best known crosslinkers for linking chitosan chains are formaldehyde, epichlorohydrin, glutaraldehyde, and tripolyphosphate [21]. Chitosan in hydrogel form is also used as an adsorbent for pollutant removal [22] . Therefore, scientists combine chitosan with polymeric materials such as polyethylene glycol [23], polyvinyl alcohol (PVA, bentonite [24] and zeolite [25]). The authors of [26] reported of chitosan-polystyrene-Zn nanocomposites by precipitation method and after characterization, they likened the efficiency of nanocomposite in nitrate ion removal b

batch and steady-state precipitation methods. A lanthanum encapsulated chitosan-kaolin composite was proposed by Thagira Banu et al. to remove nitrate ions from wastewater [27].
In view of the above, we have functionalized 50,000 Da chitosan with 2,2-(ethane-1,2-diylbis(oxy))dibenzaldehyde. The dialdehyde was synthesized by us previously based on salicylic aldehyde and 1,2-dibromoethane. The reaction scheme is presented below.





Then we modified the obtained gel with magnetite nanoparticles. Fe3O4 nanoparticles were obtained by chemical coprecipitation reaction of Fe+2 and Fe+3 iron salts. The obtained nanoparticles were stabilized with CTAB molecules and analyzed by NMR, FTIR, XRD. The morphology and composition of prepared nanostructures were investigated by transmission electron microscopy.

The structure of obtained dialdehyde have been proven by NMR spectroscopy. ^{1}H NMR spectrum (Fig.1a) of compound 1: (DMSO-d6, d, ppm), 4.57s (4H, 2OCH2), 7.077.12t(2H,Ar,J=9Hz),7.31–7.34d(2H,Ar,J=9Hz),7.64–7.69t (4H,Ar,J=9Hz),10.29s(2H,COH).^{13}C NMR spectrum of compound 1: (DMSO-d6,d,ppm),67.87(2OCH2),114.61 (2CH, Ar), 121.58 (2CH, Ar), 124.97 (2C, Ar), 128.02 (2CH, Ar), 136.85(2CH,Ar), 161.28(2C,Ar), 189.60(2COH).Found,%:C 71.04;H5.11.C16H14O4.Calculated,%:C71.11;H5.19.

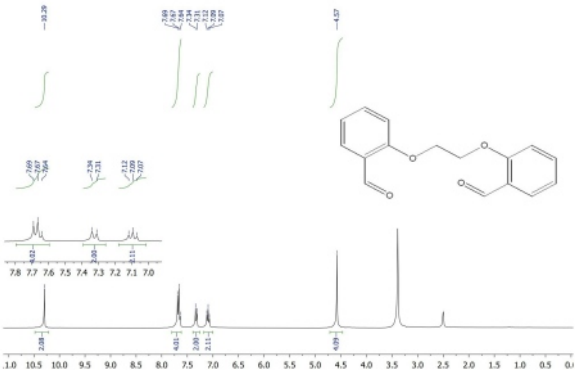


Fig 1(a) ^{1}H NMR spectra of 2,2-(ethane-1,2-diylbis(oxy))dibenzaldehyde

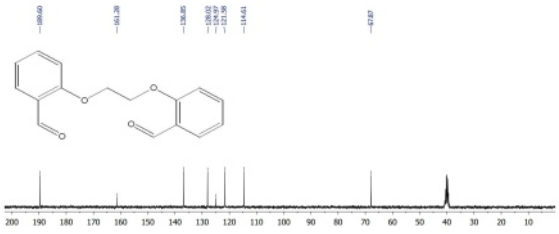


Fig 1(b) ^{13}C NMR spectra of 2,2-(ethane-1,2-diylbis(oxy))dibenzaldehyde

The functionalization of chitosan with synthesized dialdehyde led to preparing of the gel, that further was conjugated with Fe3O4 NPs. The figure 2 presents the FTIR spectra of pristine gel and gel@Fe3O4. As it can be seen from the spectra C–H stretching of aromatic ring pick reveal at 2364 cm^{-1} and C=C stretching of benzene ring at 1515 cm^{-1} . The 1636 cm^{-1} peak corresponds to imine bond (CH=N stretching) ,the 542 cm^{-1} peak represent Fe–O stretching

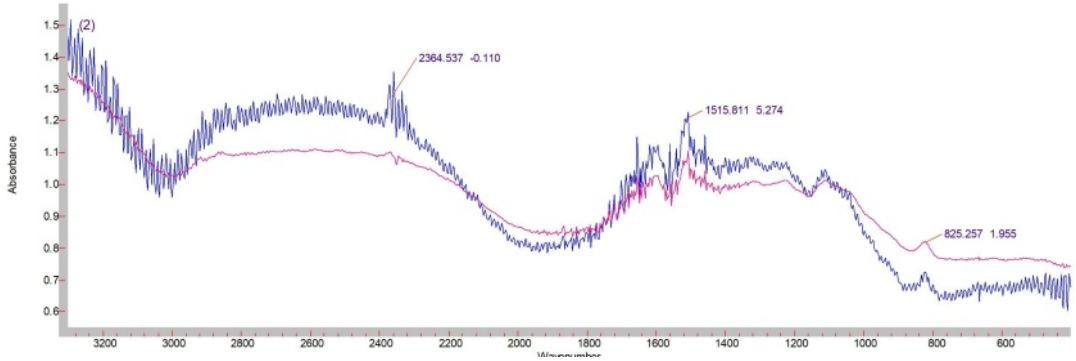


Figure 2. FTIR spectra of gel (red line), nanostructures gel@Fe3O4 (blue line)

The morphology of the gel and gel@Fe_3O_4 is presented by TEM images has been shown on the Figure 3. The TEM images of pristane gel Figure 3(a) reveals crumbly morphology of chitosan functionalized with dialdehyde. The Figure 3(b) represents the morphology of the gel conjugated with Fe_3O_4 nanoparticles. The dark regions on the spectra demonstrates the agglomeration of the Fe_3O_4 in the body of the gel.

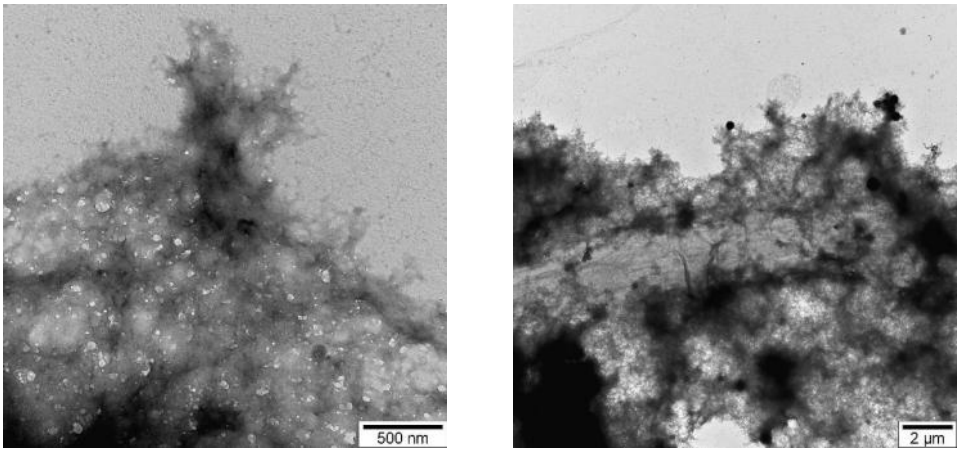


Figure 3(a) TEM image of the pristine gel; (b) TEM image of the gel@Fe_3O_4

The analyzed sample (green line) can be referred to gel@Fe3O4 nanoparticles of cubic structure because the presence of characteristic peaks at 30.131, 38.5361, 43.171, 59.071, 63.751. All these

peaks correlate with the standard pattern of Fe_3O_4, indexed in the ICDD (PDF-2/Release 2011 RDB) DB card number 01-075-0449 for the magnetite phase. The red line is the XRD spectra of chitosan indicating the standard peak 20.65 that showing crystalline form of biopolymer. The blue line is the XRD of gel that showing how the sharp peak became more gentle, indicating that the modification produced a more amorphous structure.

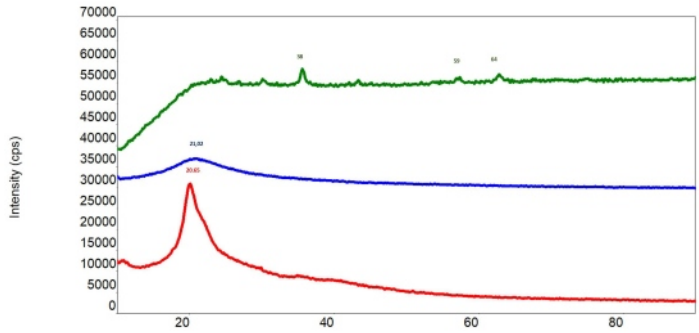


Figure 4. XRD pattern of gel

8. Conclusion

The synthesis of Schiff base and nano-ensemble were obtained by reaction of nucleophilic substitution followed by condensation of chitosan with 2,2-(ethane-1,2-diylbis(oxy)) di-benzaldehyde and further conjugation with nano magnetite. This modification of gel and gel@Fe_3O_4 were confirmed by several methods including TEM, NMR, FTIR, XRD spectroscopy. FTIR and XRD spectra showed that biopolymeric nano-ensemble underwent significant changes in comparison with chitosan. These changes included formation of imine fragment and changing the crystalline structure into the amorphous respectively. Modification of gel@Fe_3O_4 allowed for increasing in intra- and inter-molecular cavities further improving adsorption properties. The obtained structures have a great potential as adsorbent that can be used for treatment of oil-contaminated water from organic impurities and heavy metals.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research.

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