

Using mesoporous silica alternate nanomaterials in adsorption of phenols from aqueous solutions

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ABSTRACT

For efficient adsorbents of hazardous phenols from samples of waste, composite materials utilizing mesoporous silica and organic ligands were used. The 4-amino antipyrine (4-AAP) ligand has been effectively conjugated to the mesoporous nanoparticles and adsorbs phenols under appropriate conditions. The scanning electron microscope (SEM), X-ray diffraction, and N₂ adsorption/desorption isotherms process have been used to research this modern adsorbent content. The data highlighted that the proposed sensor, as per its selectivity, response, financially savvy and eco-accommodating method is highly appropriate for phenols collecting from polluted water. A batch process was used: 50 ml of 50 mg/L of each phenolic solutions at pH=8.0 with (zwitterionic buffer HEPES), was introduced to 100 mg 4-AAP sensor, then the mixture was submitted to filtration and the remaining phenols specified by Gas Chromatography in the supernatant solution. The sorbent capacity was 151.05, 82.03 and 83.47mg of phenol, m-cresol, o-cresol and quinol per gram of 4-AAP sensor, respectively with a correlation coefficient range of 0.998-0.999.

1. Introduction

Phenol is a characteristic natural compound which is extensively used in organic preparations [1] or, for example, in separating chemistry, utilizing resins of phenol that emit phenol into the air and water [2]. Phenol is likewise a health and ecological peril [3], for instance coal tar and creosote like oil based Products contain phenol that are emitted into the atmosphere by wood burning and exhaust in cars. [4]. Decomposition of natural organic matter produces phenol, which can be processed by benzene until it reaches the human body [5]. Phenol will log into the body through the mouth, skin, eyes, eyes, and respiratory course.

As seen in animal models, Phenol can function on Various reactions, extremely nature-causing tumors and tetrogenicity [6]. Phenol can contaminate food and can cause minor, acute, sub-acute signs that end in death. Nausea, puke, diarrhea and sweating, prolonged salivation, fever, vertigo, and dark brown urine are caused.

Gastrointestinal inflammation, main nervous system, cardiovascular impacts are caused by sustained exposure to phenols [7,8]; therefore, seeking a cheap and efficient approach for purifying water is crucial and important.

In the other hand, another research analysis suggested that adsorption techniques could be an efficient way for clearance of a number of organic and inorganic contaminants by three pathways from waste water, i.e., physical adsorption, chemical adsorption and ion exchange adsorption [9]. But the water had original purity and durability since pollutants were extracted by the adsorption process using adsorbents; thus, the production of modern pollutant adsorbents has increasingly formed a study hotspot [10–12]. Due to their high adsorption potential for organic compounds, different activated carbons and silicate clays operate as the most commonly used adsorbents.

In 1943, Emerson first suggested the use of 4-aminoantipyrine ligands for colorimetric phenolic substance determination. We manufactured a mesoporous, colorimetric, fluorescent sensor on silica nanoparticles as a mesoporous geometry Substrate in this article. Then, we used the sensor to detect phenols in water. The 4-AAP sensor was engineered to be water-stable, mesoporous

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silica nanoparticles by direct decoration of the 4-aminoantipyrine ligand.

2. Experimental

2.1 Materials and methods

For all experiments, Milli-Q water was utilized. 4-aminoantipyrine ligand (4-AAP), Cetyltrimethyl-ammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), Calcium Carbonate salt (CaCO_3), HCl, (Phenol, o-Cresol, m-Cresol) and potassium ferricyanide (III) salt were purchased from Sigma-Aldrich. Ethyl ether, ethyl alcohol, acetone, and ammonia solution ($\text{NH}_3\text{-H}_2\text{O}$ 25 wt%) were from Merck. Standard gas chromatography solutions with concentrations of 100 $\mu\text{g/ml}$ of mixture were obtained from Sigma-Aldrich. Nitrogen gas carrier was from sigma chem. company. USA. To control the pH at 8.0, it was used 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES).

2.2 preparation of Nanospheres of Mesoporous Silica (MSNs)

The mesoporous silica nanoparticles were fabricated as reported in the ref [13–16]. Shortly MSNs synthesized by mixing a 0.5 g CaCO_3 dispersion solution into 100 ml purified water, after that adding 0.5 g CTAB and 40 ml acetone with stirring, then adding 20 ml diethyl ether. 2.5 ml of TEOS was dropped slowly after vigorous stirring, accompanied by the addition of 1.5 ml of NH_3 (25% wt percent). The particles have been obtained by filtration. Next, 0.1M HCl was agitated again for one hour in 200 ml. Lastly, the synthesized particles were filtered and then dried for 24 h at 80 °C. The finished product has been calcinated for 8 h at 550 °C.

2.3 4-aminoantipyrine Sensor synthesis

The direct immobilization method was used in 4-AAP solid sensor fabricating by adding 30 mL of ethanol solution that includes 0.12 g of 4- AAP to 1 g of MSN and stirred for eight hours. With bi-distilled water, the produced 4-AAP sensor was softly washed and then the dry sensor was removed to grind well.

2.4 Instruments

To investigate the crystal structure of the samples, patterns of a wide angle X-ray diffraction (WAXRD) have been assessed utilizing Bruker D8 Discover diffractometer at 40 kV, an 45 mA. The isotherms for adsorption/desorption were obtained via Quantachrom Autosorb system at 77 K. The specimens have been outgassed at 200°C for 2 h. Calculations of the BET surface areas were made from N_2 adsorption data. A field-emission scanning electron microscopy (FESEM) (Hitachi S-4300) that conducted at 20 keV was assessed.

Phenol concentrations were obtained by Hewlett-Packard (HP) 5890 Series II Gas Chromatography with a column of capillaries that has a Nickel 63 flame ionization detector at 270 °C. The transporter gas was nitrogen, Extraction has been achieved with H_2SO_4 by changing pH (1-2) and extracting 3 times using 60 ml of CH_3Cl . Rotatory

evaporation was conducted using the APHA process for evaporation [17] pre and post sensor treatment.

3. Results and discussion

The morphology and structure of Nanospheres of Mesoporous Silica (MSNs):

Wide edge X-ray diffraction (WAXRD) revealed a strong peak of diffraction in the region of $2\theta = 17\text{--}30$ (Fig.1), that displayed standard ranges of electronic density [18]. The mesoporous structure was not altered by the load of the 4-AAP to the MSNs surface.

As a consequence of N_2 adsorption data, MSNs and the 4-AAP sensor samples demonstrated type IV, and wide-ranging hysteresis loop at $p/p_0 = 0.4\text{--}1.0$.

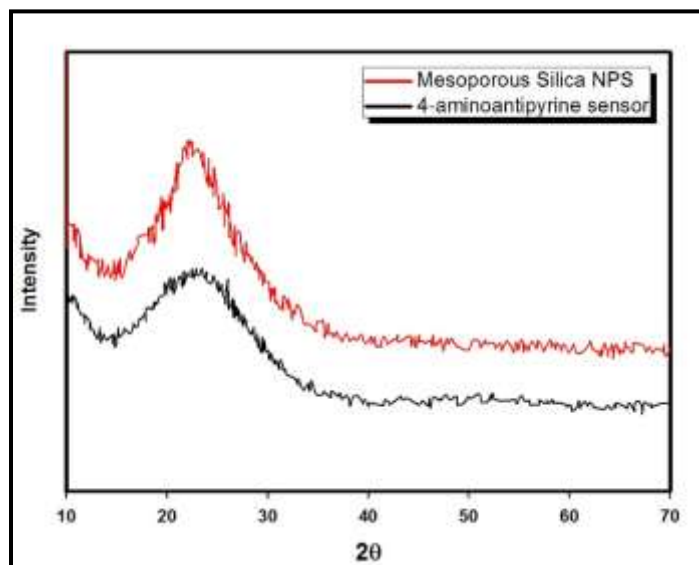


Fig. (1): wide-angle XRD (WAXRD) patterns of the calcined MSNs and 4-AAP sensor samples.

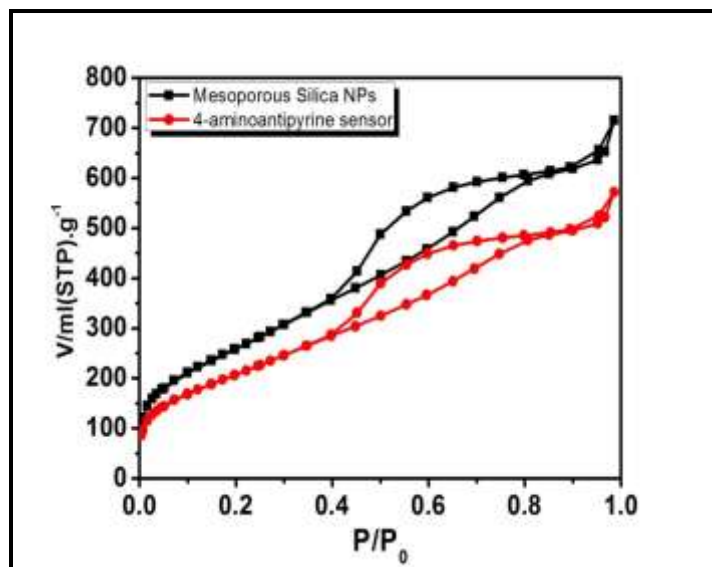


Fig. (2): Nitrogen adsorption isotherms of MSNs and the 4-AAP sensor.

Fig. 2 exhibited the calculated value of specific surface area (S_{BET}) of the MSNs was $970.95 \text{ m}^2/\text{g}$, and upon load of ligand moieties it reduced to $776.76 \text{ m}^2/\text{g}$, this outcome shows that the 4-AAP sensor preserves the MSNs mesoporosity.

FESEM images of both the bare and modified MSNs are revealed in (Fig. 3a, b). It is obvious that the two

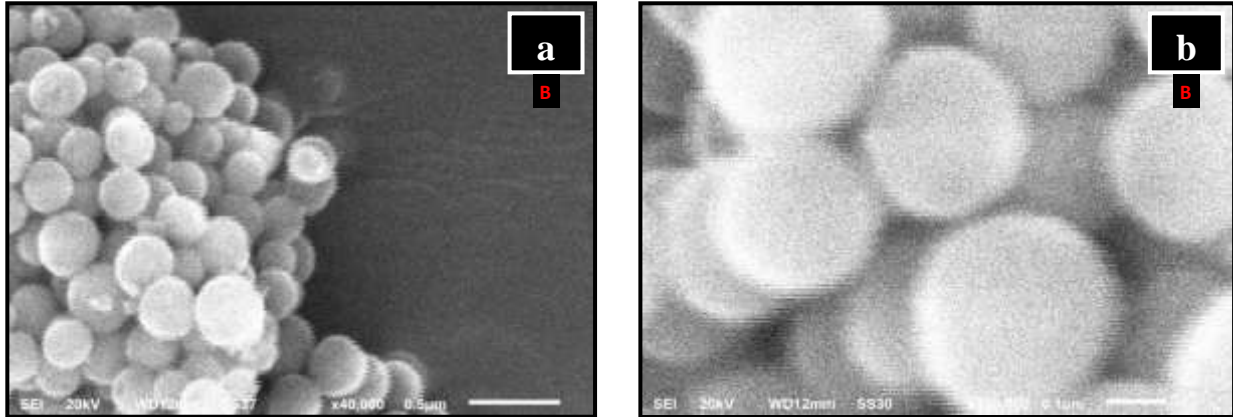


Fig. (3 a, b): FESEM images of the MSNs (a) and 4-AAP sensor (b).

Adsorption capacity

Sorption capacity is a fundamental element since it specifies the quantity of sorbent needed from a particular solution for the analyte quantitative enhancement. To assess the 4-AAP sensor's adsorption capacity, A batch process was used: 50 ml of 50 mg/L of each phenolic solutions at $\text{pH}=8.0$ with (zwitterionic buffer HEPES), was introduced to 100 mg 4-AAP sensor, then the mixture was submitted to filtration and the remaining phenols specified by Gas Chromatography in the clear solution. The sorbent capacity was 151.05, 82.03 and 83.47 mg of phenol, m-cresol, and o-cresol per gram of 4-AAP sensor, respectively.

The effect of various phenolic compound concentrations on the capacity of adsorption has also been observed (Fig. 4-6). According to the following equation, the Langmuir isotherm was expressed at fixed temperature by coverage of phenol on the 4-AAP sensor [19]:

$$C_e/q_e = C_e/q_m + 1/K_L q_m$$

At which C_e is the phenolic compounds concentration at equilibrium in solution (mg/L), q_e is the phenolic compounds amount that have adsorbed at equilibrium on the 4-AAP sensor (mg/g), q_m is the adsorbed phenolic compounds amount to produce a monolayer coverage (mg/g), and K_L is the adsorption of Langmuir equilibrium constant.

Our studies have shown that the capacity of equilibrium adsorption rises with rising phenolic compound concentrations. From the adsorption experiment, the C_e/q_e vs C_e plot produce a straight line and this shows the development of a monolayer coverage of phenolic compounds on the 4-AAP sensor surface (Fig. 4-6 insert).

materials function as nanostructures in the 300-400 nm region. It additionally proposed that after distribution, there was no seen change in the design of our 4-AAP all along the surface, so these observations are compliant with the findings of XRD.

From the intercept and slope of the linear ranges of the Langmuir plots, the constant of Langmuir coverage (K_L) and functional adsorption capacity (q_m) were obtained, correspondingly. The linear curves of adsorption illustrate that it is possible to extract a wide variety of phenolic compound concentrations. A straight plot has a coefficient of correlation of 0.998-0.999 reveals that the Langmuir isotherms of adsorption describe the phenolic adsorption experiments for phenolic compounds (phenol, m-cresol and o-cresol) the data are collected in Tables (1-4).

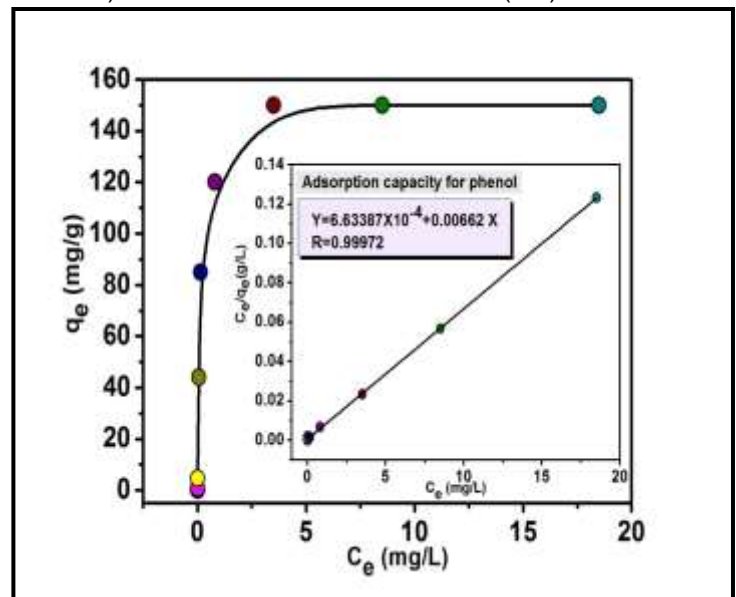


Fig. (4): The Isotherms for the adsorption of different concentrations of phenol compound. The insets show the linear form of the Langmuir plots for the adsorption of phenol compound onto the 4-AAP sensor adsorbent at room temperature.

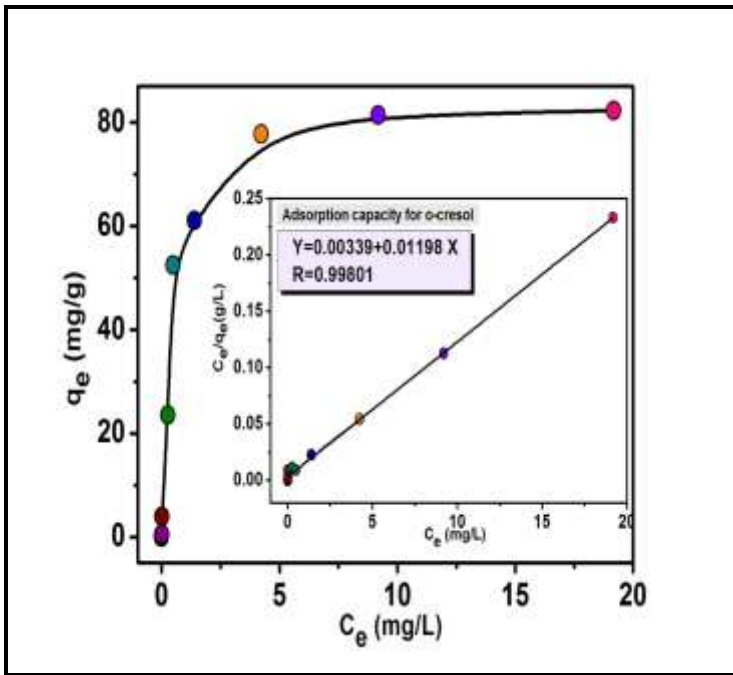


Fig. (5): The Isotherms for the adsorption of different concentrations of o-Cresol compound. The insets show the linear form of the Langmuir plots for the adsorption of o-Cresol compound onto the 4-AAP sensor adsorbent at room temperature.

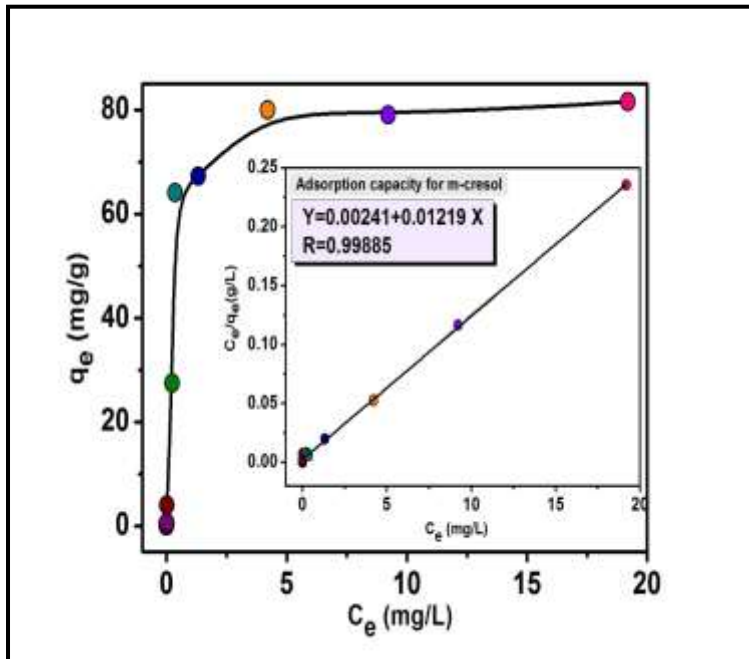


Fig. (6): The Isotherms for the adsorption of different concentrations of m-Cresol compound. The insets show the linear form of the Langmuir plots for the adsorption of m-Cresol compound onto the 4-AAP sensor adsorbent at room temperature.

Table (1): The parameters of Isotherm for the adsorption of different concentrations of Phenol compound.

[Phenol] (ppm)	C _e	q _e	C _e /q _e
0.0001	0.000000025	0.0099975	2.50063x10 ⁻⁶
0.0005	0.0000005	0.04995	1.001x10 ⁻⁵
0.001	0.00005	0.095	0.0005263
0.005	0.000125	0.4875	0.000256
0.01	0.0017	0.83	0.0020481
0.05	0.003	4.7	0.0006382
0.5	0.06	44	0.0013636
1	0.15	85	0.0017647
2	0.8	120	0.0066666
5	3.5	150	0.0233333
10	8.5	150	0.0566666
20	18.5	150	0.1233333

Table (2): The parameters of Isotherm for the adsorption of different concentrations of o-Cresol compound.

[o-Cresol] (ppm)	C _e	q _e	C _e /q _e
0.0001	1.79x10 ⁻⁸	0.00999821	1.79032x10 ⁻⁶
0.0005	7.75x10 ⁻⁸	0.04999225	1.55024x10 ⁻⁶
0.001	0.0000621	0.09379	0.0006621
0.005	0.000526	0.4474	0.0011756
0.01	0.004731	0.5269	0.0089789
0.05	0.01032	3.968	0.0026008
0.5	0.265	23.5	0.0112765
1	0.4751	52.49	0.0090512
2	1.389	61.1	0.0227332
5	4.223	77.7	0.05435006
10	9.186	81.4	0.1128501
20	19.1775	82.25	0.233161

Table (3): The parameters of Isotherm for the adsorption of different concentrations of m-Cresol compound.

[m-Cresol] (ppm)	C _e	q _e	C _e /q _e
0.0001	1.53x10 ⁻⁸	0.00999847	1.53023x10 ⁻⁶
0.0005	0.000000071	0.0499929	1.4202x10 ⁻⁶
0.001	0.000059	0.0941	0.000626993
0.005	0.000498	0.4502	0.001106175
0.01	0.00422	0.578	0.007301038
0.05	0.00993	4.007	0.002478163
0.5	0.226	27.4	0.008248175
1	0.359	64.1	0.005600624
2	1.328	67.2	0.019761905
5	4.2	80	0.0525
10	9.21	79	0.116582278
20	19.185	81.5	0.235398773

Table (4): Analytical parameters of Langmuir adsorption isotherms for phenolic compounds.

Phenolic Compound	Slope	R	Intercept	q_m	K_L
Phenol	0.0066	0.999	0.00066	151.06	9.979
O-Cresol	0.0119	0.998	0.00339	83.472	3.533
m-Cresol	0.0121	0.998	0.00241	82.034	5.058

R: Correlation coefficient; **q_m :** the amount of phenolic compounds adsorbed to form a monolayer coverage (mg/g); **K_L :** is the Langmuir adsorption equilibrium constant.

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