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An environmentally friendly approach to the synthesis of azo dyes based on 2-naphthol using kaolin-SO_3H nanoparticles

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ABSTRACT

Kaolin-SO_3H nanoparticles were prepared *via* reaction of kaolin and chlorosulfonic acid and characterized by FT-IR, XRD, FESEM, TEM, XRF, EDS, BET and TGA. The activity of this green catalyst was probed by the synthesis of aryl diazonium salts as the starting reactant and then, their diazo coupling with 2-naphthol to form azo dyes in a solvent-free medium at room temperature. The work-up of the reaction was easy, and the catalyst was removed from the products by simple filtration. The reaction proceeded in a short time, easy purification technique, high yields, and was environmentally friendly furthering approaches to green chemistry. The products were characterized by FT-IR and NMR spectroscopy.

Keywords*:* *2-Naphthol, Kaolin-SO_3H, Nanoparticles, Diazonium salt, Diazo coupling, Solvent-free.*

1. Introduction

Many of organic solvents such as chlorinated hydrocarbons have toxic nature that threatens the environment so avoiding organic solvent during the reactions in organic synthesis leads to a clean, efficient and economical technology. The use of heterogeneous catalysts was more concerned in the area of green chemistry in the recent times [1-6], due to enhanced safety, increased efficiency, reduced costs and contamination, simplified work up and sometimes enhanced selectivity of the reaction. Towards green chemistry and clean technology, a heterogeneous catalyst can be recovered after the reaction [7-12].

In organic chemistry, azo dye compounds, are a class of dyes with certain properties which are now being considered for various aspects such as colorants for digital printing and photography [13], liquid crystals [14], chiral receptors [15], dyes for drug, food and cosmetic applications and organic synthesis [16,17]. Azo dyes are generally synthesized by the coupling reaction between diazonium salts and activated aromatic compounds such as phenols and aromatic amines. This synthetic approach has limitations such as use of instability of aryl diazonium salts at room temperature, acid–base catalyst and need of low temperature [17,18]. Nowadays, heterogeneous solid acids have resolved these limitations and improved activity and selectivity rather than individual reagents [5,12].

Kaolin is one of the most common minerals [19]. Large volumes of kaolin clays are used for the production of cement [20] and ceramics [21]. The greatest demand for kaolin is in the paper industry to produce a high-quality paper [22]. It is also used as filler for paint rubber and plastics [21]. Kaolin clay found its application in medicine, in toothpaste, in cosmetic and as a food additive [22]. Recently, a specially formulated spray is used in fruit and vegetable production to repel the insects and prevent sunburn [23]. Usually, suitable kaolin contains 70-73% of SiO_2, 18-20% of Al_2O_3, 0.4-1% of Fe_2O_3, and 0-0.8% of TiO_2 and no MnO.

In this work, kaolin-SO_3H nanoparticles used for the synthesis of some azo dyes based on 2-naphthol (Scheme 1). Due to the large surface to volume of nanostructures, solid acids are shown higher activity and selectivity than their corresponding bulk materials.

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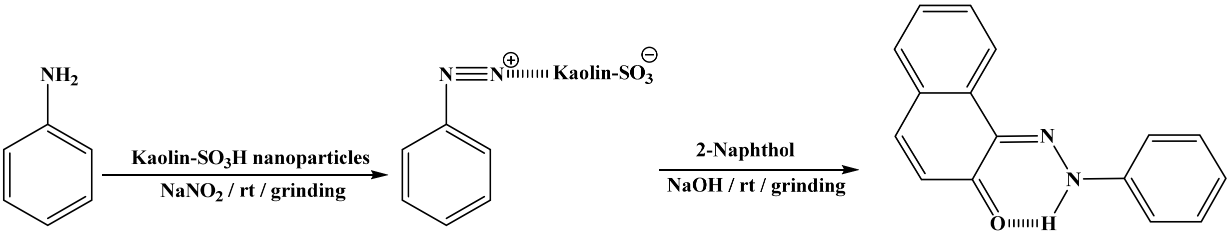


Scheme 1. Synthesis of azo dyes using kaolin-SO_3H nanoparticles at room temperature.

2. Experimental

2.1. Materials and apparatus

All Chemicals and solvents such as 2-naphhol, arylamine derivatives, chlorosulfonic acid, kaolin nanoparticles and ethanol were purchased from Fluka, Merck and Aldrich chemical companies and were used without any further purification. All of the products are known compounds which were characterized by comparison of their spectral (FTIR, ^{1}H and ^{13}CNMR), and physical data with authentic samples. ^{1}H and ^{13}CNMR spectra were recorded on a Bruker DRX-400 Avance spectrometer in $CDCl_3$ as solvent and chemical shift are expressed in δ ppm relative to tetramethylsilane. IR spectra were determined on a Nicolet Magna series FT-IR 550 spectrometer using KBr pellets. Thin layer chromatography (TLC) on commercial aluminium-backed plates of silica gel 60 F_{254} was used to monitor the progress of the reactions. Melting points were obtained with a micro melting point apparatus (Electrothermal, Mk3). The XRD patterns were collected on a Philips Xpert MPD diffractometer equipped with a Cu Kα anode (λ=1.54 Å) in the 2θ range from 10 to 80°. Elemental composition was investigated by XRF BRUKER S4 EXPLORER. Average size of kaolin-SO_3H nanoparticles was analyzed by FESEM and TEM using a Mira 3-XMU and Philips CM120 with a LaB6 cathode and accelerating voltage of 120 kV, respectively. Brunauer–Emmett–Teller (BET) surface area analysis of catalyst was done with Micromeritics, Tristar II 3020 analyzer. Quantitative elemental information (EDS) of kaolin-SO_3H nanoparticles was measured by EDS instrument, Phenom pro X.

2.2. Preparation of kaolin -SO_3H nanoparticles [24]

In a ventilated cabinet, a 100 mL suction flask containing 5g of commercial kaolin nanoparticles was equipped with a dropping funnel containing 10 mL of chlorosulfonic acid and gas inlet tube for conducting obtained HCl gas over a water vessel. Then, 25 mL of chloroform was added to the suction flask and chlorosulfonic acid was added drop-wise to the mixture with vigorously mixing at room temperature. After the addition of chlorosulfonic acid was completed, a white solid was obtained. The solid was filtered and washed with chloroform and dried at room temperature. The kaolin-SO_3H nanoparticles was obtained with 98 % yield and characterized by FT-IR, XRD, SEM, TEM, XRF, TGA, EDS and BET techniques.

2.3. A typical procedure for the diazotization and azo coupling reactions

In a mortar, 4-chloroaniline (2 mmol), sodium nitrite (3 mmol) and kaolin-SO_3H (0.05 g) were ground for 5 minutes. Then, a few drops of water was added to the mixture with grinding for 15 minutes (mixture A). In another mortar, a mixture of 2-naphthol (2 mmol) and NaOH (10 mmol) was ground for 10 minutes (mixture B). Then, the mixture B was added to mixture A with vigorous grinding. The progress of the reaction was monitored by TLC (petroleum ether–ethyl acetate **5**:**1**). The crude product was resolved in acetone and the solid acid catalyst was separated by simple filtration. After evaporation of acetone, the crude azo products were purified by recrystallization in EtOH. The results of the synthesis of azo dyes by kaolin-SO_3H nanoparticles are summarized in Table 1.

3. Results and Discussion

3.1. Characterization of kaolin-SO_3H nanoparticles

In order to identify the molecular structure of kaolin-SO_3H nanoparticles, FT-IR analysis of the kaolin nanoparticles and kaolin-SO_3H nanoparticles were compared (Fig. 1). In FT-IR spectrum of kaolin, many bands at 3686 and 3620, 1114, 990, 909, 791and 752 cm^{-1} were existed. However in the kaolin-SO_3H nanoparticles, in addition to the above mentioned bands, a band at 1160 cm^{-1} and a very broad band at 2700-3400 cm^{-1} were appeared. The broad band at 1160 cm^{-1}and a very broad band at 2700-3400 cm^{-1} verify the O=S=O and –SO-H vibrations on kaolin-SO_3H, respectively. In the 990 cm^{-1} and 640 cm^{-1} region, main functional groups were Si-O and Al-OH.

Table 1. Synthesis of azo dyes in the presence of kaolin-SO_3H nanoparticles as catalyst and at room temperature.

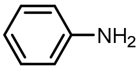
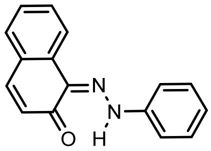
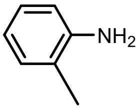
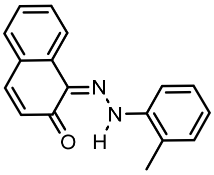
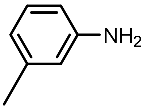
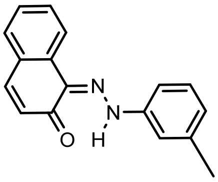
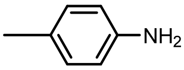
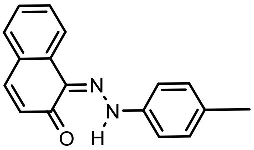
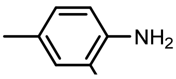
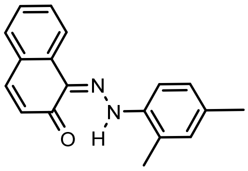
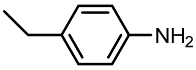
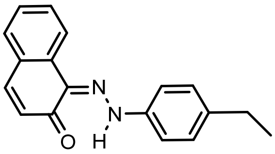
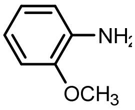
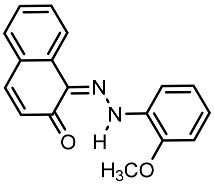
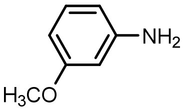
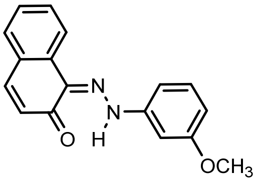
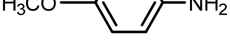
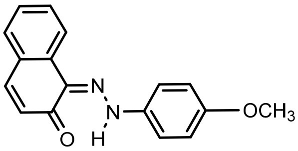
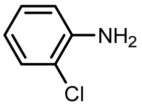
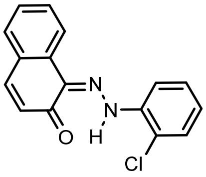
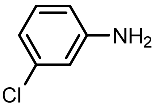
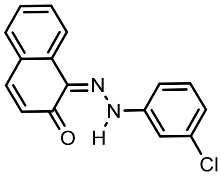
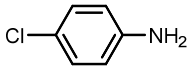
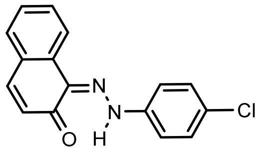
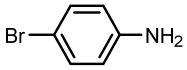
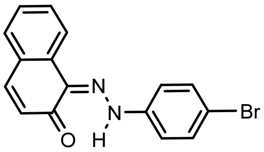
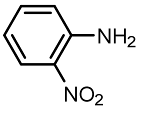
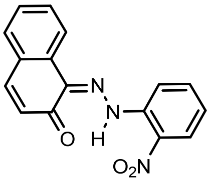
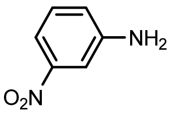
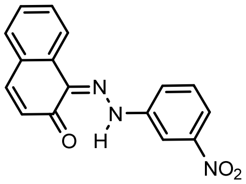
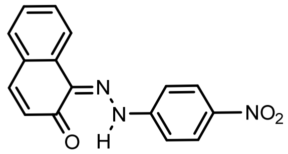
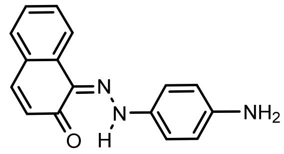
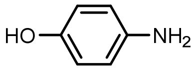
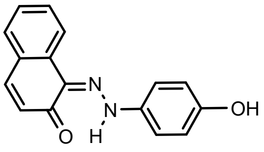
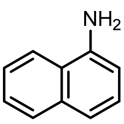
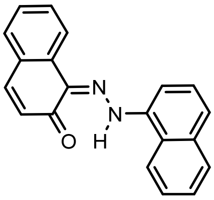
Entry	Aryl amine	Product	Yield[a]	m.p. (°C)		Ref.
				Found	reported	
1			88	130-132	131-132	[25]
2			90	129-131	131	[26]
3			95	115-117	115-118	[25]
4			95	139-141	142	[26]
5			89	183-186	184-186	[26]
6			82	76-78	75-76	[27]
7			87	180-182	181-183	[27]
8			90	121-123	116-118	[12]
9			85	133-135	136-137	[28]

Table 1. *(Continued).*

10			88	169-170	166	[26]
11			79	152-154	152-154	[26]
12			83	161-163	169-171	[28]
13			87	155-157	156-157	[28]
14			85	241-242	245	[26]
15			78	201-203	206-207	[28]
16			80	244-247	251-253	[25]
17			75	295-297	300-302	[29]
18			89	195-196	191-193	[29]
19			65	141-144	-	-

[a]Isolated yield.

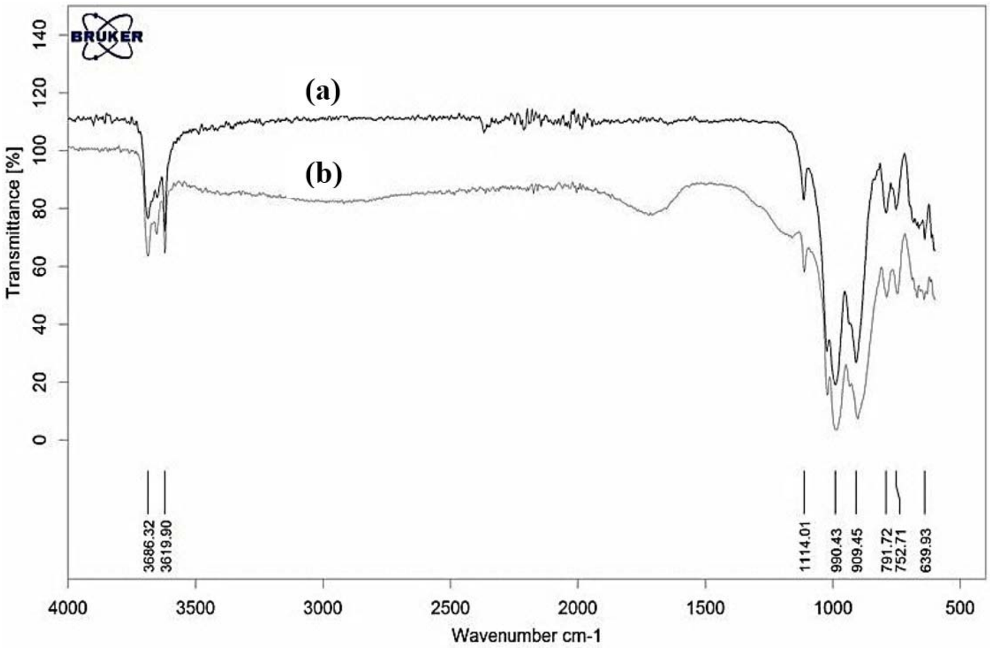


Fig. 1. FT-IR (ATR) spectrum of (a) kaolin nanopaticles and (b) kaolin–SO_3H nanoparticles.

Fig. 2 shows the XRD powder diffraction pattern of kaolin-SO_3H nanoparticles. As shown in this figure, incorporation of -SO_3H leads to some changes in the diffractogram of kaolin nanoparticles. In the diffractogram of kaolin nanoparticles in 2θ from 62 to 74, nine peaks but in kaolin-SO_3H nano particles, only three peaks (at 70.60, 72.67 and 74.08) are existed. In kaolin-SO_3H nanoparticles, three peaks in 2 θ from 20 to 25 were disappeared. Other peaks in kaolin and kaolin-SO_3H nanoparticles diffractograms are in the same position. The sharpness of peaks in the kaolin-SO_3H nanoparticles diffractogram shows crystalline form for this catalyst.

Field emission scanning electron microscopy (FESEM) and transition electron microscope (TEM) images of the kaolin-SO_3H nanoparticles are displayed in Fig. 3 (a-b). These images clearly showed the amorphous surface morphology of the kaolin-SO_3H nano particles with an average size distribution of 15 nm.

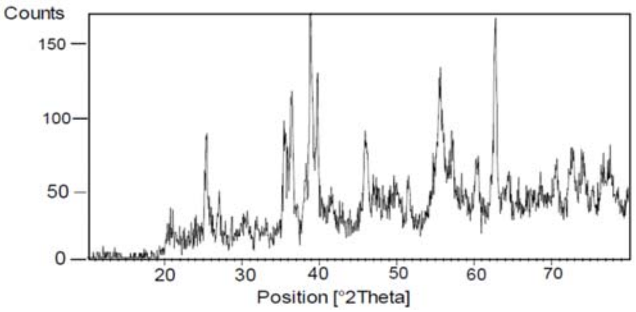


Fig. 2. X-ray diffraction (XRD) pattern of kaolin-SO_3H nanoparticles.

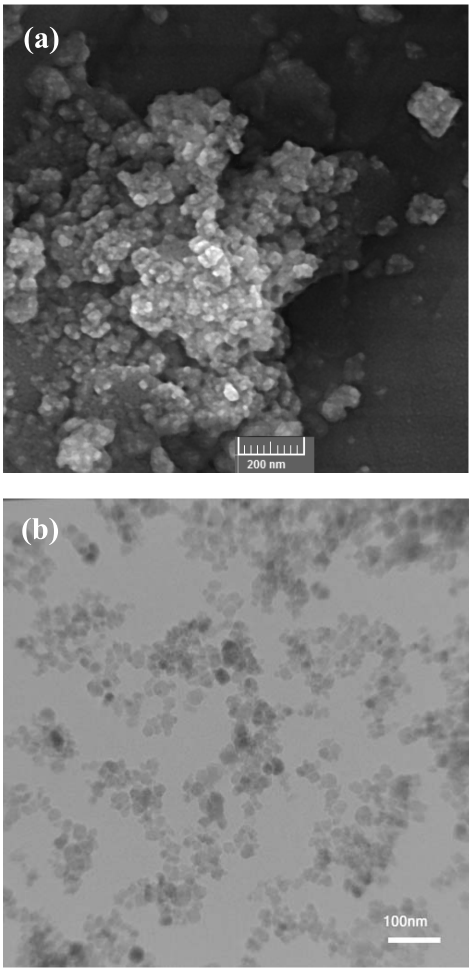


Fig. 3. (a) FESEM and (b) TEM photographs of kaolin-SO_3H nanoparticles.

TG-DTG curves of starting kaolin display a strong peak at 517 °C, which is due to dehydroxylation of kaolin within the 450-600 °C temperature range resulting in a weight loss of 15.34 % and formation of meta-kaolin. The peak on the TG-DTG curve at approximately 980 °C is an evidence of the breakdown of the meta kaolin structure and the formation of mullite. Thermal gravimetric analysis (TG-DTG) pattern of kaolin-SO_3H nanoparticles was detected from 25 to 750 °C (Fig. 4). The catalyst is stable up to 100 °C and only 5 % of its weight was reduced in 120 °C. One endothermic processes were accrued between in 130°C due to decomposition of $-SO_3H$ group and elimination of SO_2 and H_2O from catalyst. Another endothermic processes in 530 °C caused mass changed equal to 5 % due to dehydroxylation of kaolin.

The X-ray fluorescence spectrum of kaolin-SO_3H nanoparticles showed that 15.9% of SO_3, 43% of SiO_2 and 30.5% of Al_2O_3 were presented in the composition of kaolin-SO_3H.

The percentage of S, O, Si and Al in kaolin-SO_3H nanoparticles is shown in Table 2. The percentage of each element in nanocatalyst was approved by EDS analysis data (Fig. 5).

Specific surface area of catalyst was measured by BET theory. The single point surface area at P/Po= 0.983 is 7.59 m²/g, while the mean pore diameter is 20.601 nm and the total pore volume is 3.909 $cm^3\ g^{-1}$. The N_2 adsorption isotherm of catalyst is shown in Fig. 6.

Acidity of the catalyst was compared with kaolin. The pH of 0.05 g of commercial kaolin or kaolin-SO_3H in 5 mL of distilled water is 6 and 3.4, respectively. The acidic capacity of catalyst was determined via titration of 0.05 g of it with 12.16 mL of 0.009 N of NaOH and was 2.268 meq/g H^+.

3.2. Reusability of the catalyst

One of the outstanding advantages for the solid acid catalysts are their reusability and stability which makes them valuable for commercial applications. Thus, after completion of the reaction, the catalyst was separated. The reaction mixture was washed with chloroform (2×3 ml) and the catalyst was separated by filtration. The recovered catalyst was washed with chloroform (3×10 mL) and dried at room temperature without further purification to use for the next run in current reaction under equal condition. It was found that the catalyst could be reused for five times (Yields were 99, 95, 87, 72 and 60%, respectively) without any considerable loss of its activity.

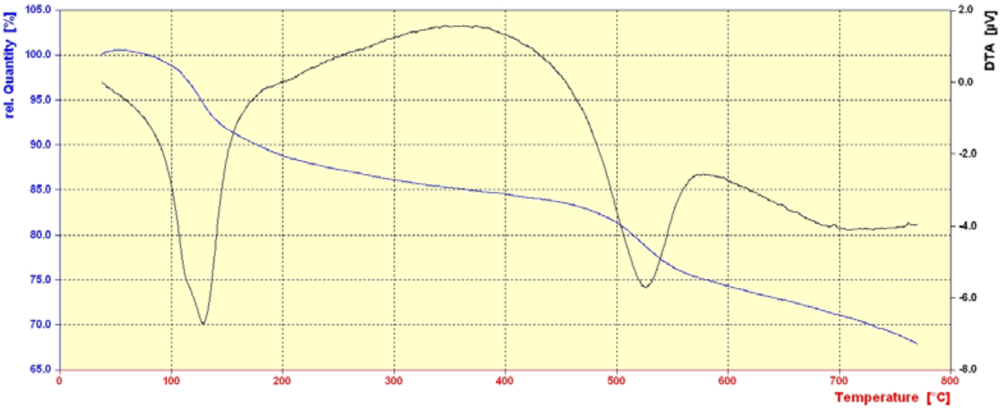


Fig. 4. Thermal gravimetric analysis (TGA-DTG) pattern of kaolin-SO_3H nanoparticles.

Table 2. The results of EDS analysis of kaolin-SO_3H nanoparticles.

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
O K	249.75	1.1405	61.06	0.28	73.17
Al K	49.20	0.8817	15.56	0.17	11.06
Si K	58.99	0.7736	21.26	0.21	14.51
S K	5.70	0.7514	2.12	0.09	1.27
Total			100.00		

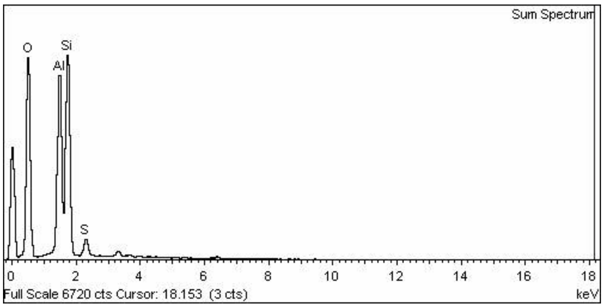


Fig. 5. EDS spectra of kaolin-SO_3H nanoparticles.

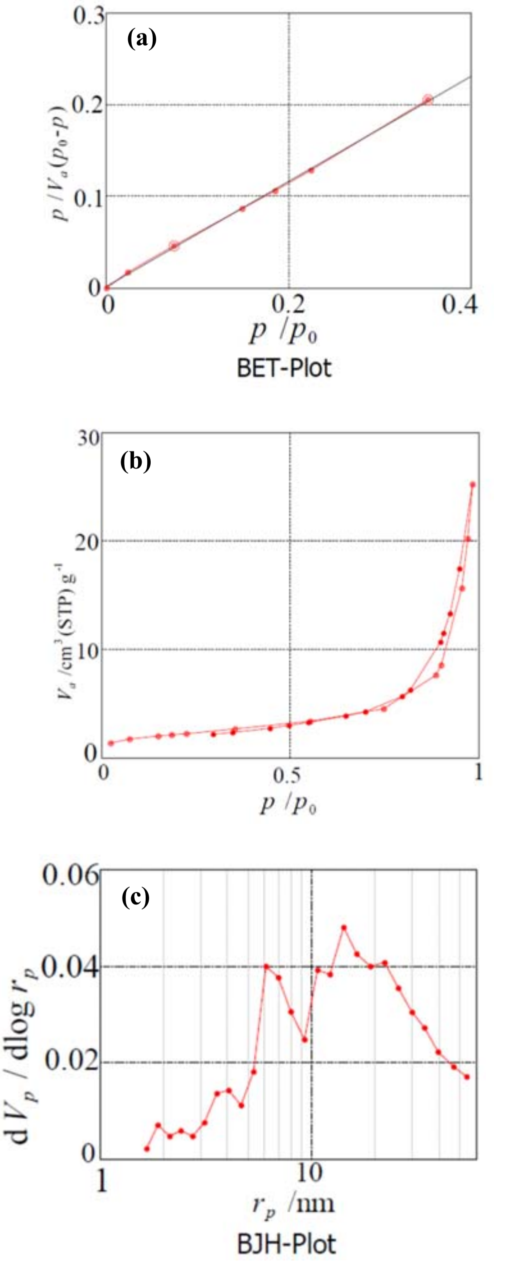


Fig. 6. (a) BET (Brunauer–Emmett–Teller), (b) adsorption-desorption isotherm and (c) BJH (Barrett-Joyner-Halenda) plots of kaolin-SO_3H nanoparticles.

3.3. Stability of diazonium salt at room temperature:

Diazonium salts play an important role as intermediates in the organic synthesis, such as azo dyes. However, diazonium salts are thermally unstable and separation of the acidic catalysts from the reaction medium is difficult. Therefore, we decided to solve these limitations by developing a green and facile procedure for the synthesis of azo dyes in the presence of a heterogeneous solid acid nano catalyst. We studied the stability of diazonium salt supported on kaolin-SO_3H nano particles which obtained from diazotation of 4-chloro and 4-methylaniline. It was found that diazonium salt supported on kaolin-SO_3H nano particles is stable for about 6 months. The results of study on stability of diazonium salt at room temperature summarized in Table 3.

4. Conclusions

A green and highly effective methodology for the synthesis of azo dyes was developed by solvent-free diazo coupling of aryl diazonium salts with 2-naphthol at room temperature. Using kaolin-SO_3H nanoparticles as a heterogeneous super solid acid in diazotization step and solvent-free procedure caused the experimental simplicity, compatibility with environment, no use of special conditions such as low temperature, efficient yields, short reaction times and made this procedure attractive to synthesize a variety of these compounds.

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Table 3. The results of study on stability of diazonium salt at room temperature.

Entry	Amine	Yield (%) [month]					
1	4-Methylaniline	94 [1]	90 [2]	86 [3]	79 [4]	60 [5]	48 [6]
2	4-Chloroaniline	91 [1]	88 [2]	80 [3]	69 [4]	52 [5]	40 [6]

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