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Synthesis, characterization and sorption studies of β-naphthol azo dyes on wool fabric

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Abstract: A new nano silicagel supported by thionyl chloride as a solid acid was synthesized and used to increase the production yield of dye to affect the efficient diazotization of arylamines. The obtained diazonium salts were then coupled, using standard experimental procedures, in order for to anilines and naphthols to afford the requisite azo dyes in good yield. The diazotization and subsequent azo-coupling generated the related azo dyes at low temperature in short reaction times with no use of dense liquid acids. Structures of the dyes were fully characterized by spectroscopic techniques (UV, IR, ^{1}H and ^{13}C NMR). In addition, the adsorption properties of the synthesized dyes on wool fabric were also determined. The adsorption isotherm was tested by fitting the adsorption data with Langmuir and Freundlich isotherms. The results indicate that the Langmuir model appears to fit the adsorption better than the Freundlich model.

Keywords: Synthesis, Azo dye, Adsorption, Isotherm, Wool.

Introduction

Azo compounds are considered to be the most widely used class of industrial synthesized organic dyes due to their versatile applications in fields such as dyeing textile fiber, biological-pharmacological activities and advanced application in organic synthesis [1-6]. More than 50% of textile dyes are azoic dyes which are recognized by nitrogen π-bound [7, 8].

The usual azo dyes synthesis methods require some difficult conditions like low temperature, high pressure and also the use of dense liquid acids [9-11]. These problems can be removed by using nano solid acids. Solid acid catalysts have served as important functional materials for chemicals production. However, the processes involving conventional acids are typically associated with problems of high toxicity, catalyst waste, use of a large amount of catalyst, and difficulty of recycling. Replacement of liquid acids with solid ones is desirable in chemical industry because solid acids are environmentally friendly with respect to corrosiveness, safety, reduced waste and ease of use [12, 13].

Coloration theories are mostly based on physical chemistry of adsorption that is affected by physical elements like pressure, heat, density and electric potential over chemical reactions, combinations and products of such reactions. Results obtained from coloration tests in balanced state were presented as adsorption isotherm showing the dye density changes inside the fiber and solution measured in fixed temperature [14]. In Langmuir adsorption isotherm, adsorption took place in specific places in fibers that no other molecules absorb there after filling up the place with dye [15]. Freundlich adsorption isotherm is utilized for describing the multi-layer adsorption with inter-molecular interaction. Furthermore, the

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adsorption is accomplished as reversible on heterogeneous superficial with equal distribution of energy [16].

Several researchers have reported the diazotization of aniline derivatives [17-23]. For instance, Lyčka et al. reported the synthesis of some phenylazonaphthols in 1-butyl-3-methylimidazolium tetrafluoroborate using a coupling reaction of (4-x-benzene)diazonium tetrafluoroborates (X=H and NO_2) with 1- and 2-naphthols and their sodium salts [22]. Along the same lines, Noroozi-Pesyan et al. synthesized azo dyes via diazotization of aniline derivatives and subsequent azo-couplings in the presence of *p*-toluenesulfonic acid through grinding [23]. In this study, two azo dyes were synthesized by the diazonium coupling reaction of two different aromatic amines, using nano silicagel supported by thionyl chloride as a solid acid and the synthesized dyes were examined by UV, NMR and IR. This research also aims to evaluate the adsorption potential of wool fiber for the dyes. This helps to control the dyeing process progressively.

Results and discussion

Spectral characteristics:

The assumed structures of the synthesized dyes were confirmed by IR, ^{1}H NMR and ^{13}C NMR spectra. IR, ^{1}H NMR and ^{13}C NMR spectra of the dyes are shown in Figures **1–3**, respectively. Velasco and co-workers reported the synthesis of some phenylazonaphthols *via* different nitrates as sources of nitrosonium ion to obtain diazonium salts [24], and the acquired yields were reported in Table **1**. This research introduces a new nano silicagel supported by thionyl chloride as a solid acid that can act as increasing the production yield of dye for the efficient conversion of aryl amines to their corresponding diazonium salts. Azo-coupling of these diazonium salts afforded the related azo dyes in good yields (Figure **4**). The structures of the synthesis dyes were deduced from their elemental analyses and their IR, ^{1}H NMR, ^{13}C NMR spectra. Based on the chemical structure, the synthetic dyes can be classified as disperse dyes.

Adsorption isotherm studies:

Both of the synthesized dyes are classified as disperse dyes. However, large parts of the wool fibers are hydrophobic, so that it is possible for the dye molecule to reduce its potential energy by being adsorbed with its hydrophobic parts on the hydrophobic portions of the wool [25, 26]. Based on research results, disperse dyes are not all adsorbed by wool as surface deposits, but in certain instances can penetrate the fiber to give a dyeing with acceptable fastness properties [27]. The adsorption isotherm of the synthesis dyes are shown in Figure **5.**

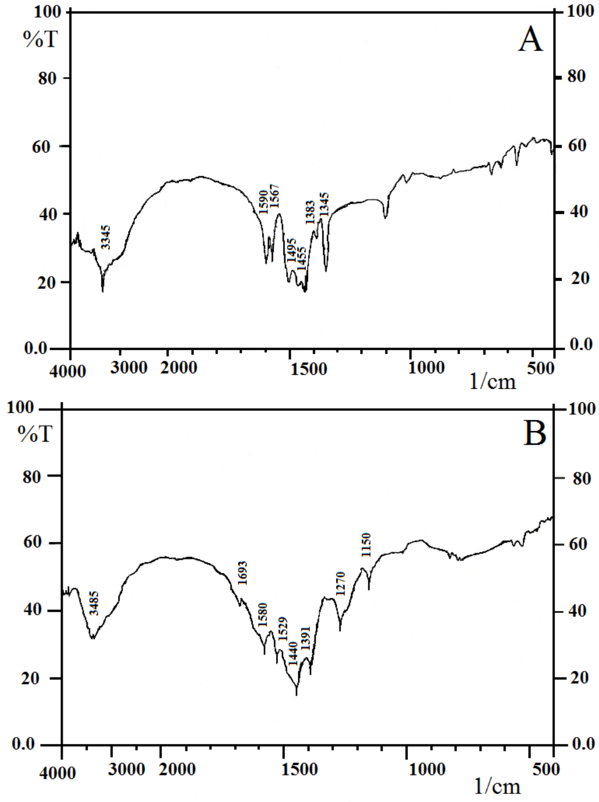


Figure 1: FTIR spectra of the synthesis dyes (A) 2-(2-Hydroxy-naphthalen-1-ylazo)-nitrobenzene and (B) 2-(2-Hydroxy-naphthalen-1-ylazo)-benzoic acid.

It is observed that the dyes uptake in fabric ($[D]_f$) continues to increase with the increase in dye concentration before it reaches the saturation point. Prior to reaching the saturation , the relationship between dye in solution ($[D]_s$) and dye uptake in fabric ($[D]_f$) can be considered as a linear function. Therefore, its slope is constant and a partition coefficient (K) of the dye between the fabric ($[D]_f$) and the dyeing solution ($[D]_s$) was obtained from the adsorption isotherm. Based on the obtained results, dye B showed better adsorption on wool in comparison with dye A. The hydrophobicity of the dye B was extended by replacement of the nitro group with carboxyl group. In order to increment the hydrophilicity of disperse dyes, some groups such as hydroxyl and carboxylic acids were added to their chemical structures. One obvious way to eliminate wool-polyester dyeing process disadvantages (two-bath process and staining of the wool) is to develop a single dye which exhibits equal affinity for both fibers of the blends. The dyes with weak carboxylic groups and molecular weights of 300-500 (g/mol) can be applied for dyeing both wool and polyester fibers with excellent leveling and very good wet-fastness properties [25, 28]. Therefore, observed enhancement on the adsorption of dye B on wool is thought to be explained on the basis of the increase in aqueous solubility of the dye.

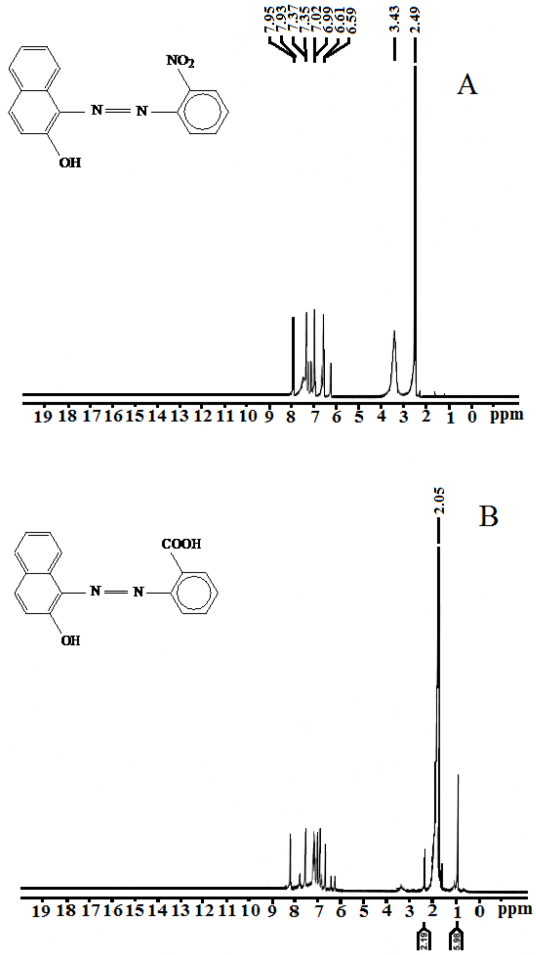


Figure 2: ^{1}H NMR spectra of the synthesis dyes (A) 2-(2-Hydroxy-naphthalen-1-ylazo)-nitrobenzene and (B) 2-(2-Hydroxy-naphthalen-1-ylazo)-benzoic acid.

Results also indicated that, for dye B, the adsorption of the dye by the wool fabric reached a maximum at 60 ˚C, but at higher temperatures was rapidly desorbed into the bath. But for dye A, the dye adsorption on the wool fabric increased as the dyeing temperature increased.

The Langmuir adsorption isotherm has been applied to many sorption processes of monolayer adsorption. This model assumes that the intermolecular forces decrease rapidly with distance and the adsorption occurs at specific homogeneous sites on the adsorbent. Langmuir equation also assumes structurally homogeneous adsorbent having similar sorption sites, which are energetically identical [29]. Theoretically, a saturation value is reached for adsorption. The saturated sorption capacity can be given as shown below:

$$\frac{Ds}{Df} = \left(\frac{1}{kLqm}\right) + \left(\frac{D_s}{q_m}\right) \qquad (1)$$

where, D_s is the dye concentration (mg/dm) at equilibrium; D_f, denotes the amount of dye at equilibrium per gram of wool (mg/g); q_m, is the constant signifying limiting adsorption capacity when the surface is completely covered by dye molecules (mg/g); and kL (dm^3/mg), indicates the Langmuir constant which depends on the energy of adsorption.

Straight lines were obtained by plotting $1/D_f$ against $1/D_s$ for the adsorption of dye onto wool as shown in Figure **6**. Langmuir constants q_m and kL were obtained From the slope and intercept of such a plot (Table 2).

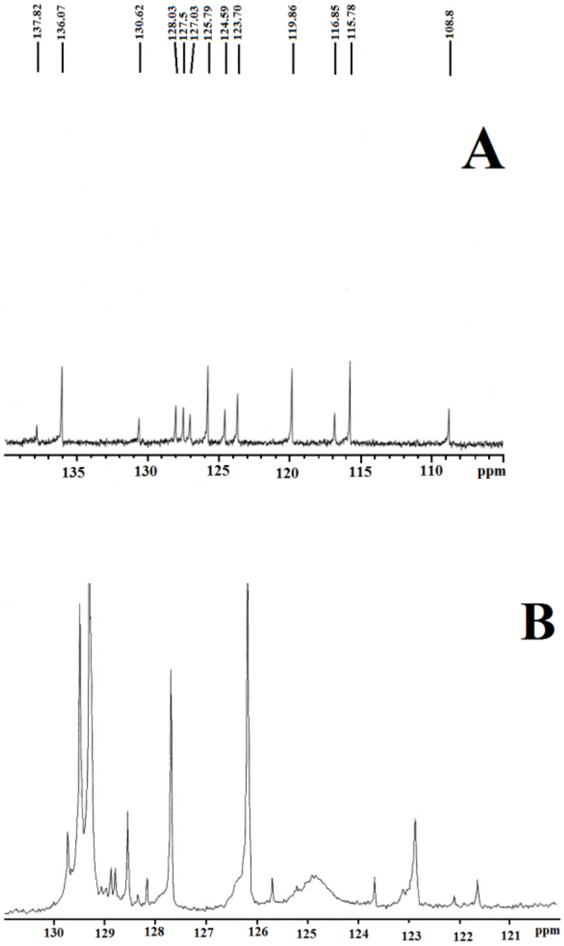
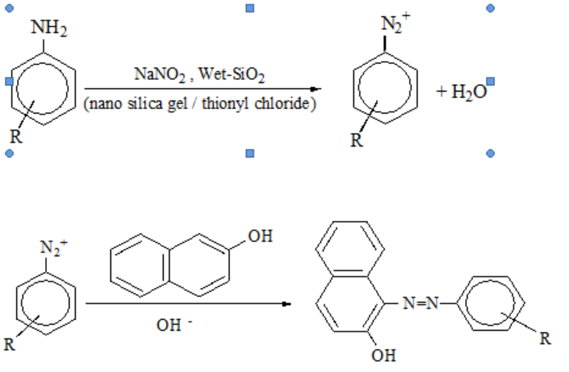


Figure 3: ^{13}C NMR spectra of the synthesis dyes (A) 2-(2-Hydroxy-naphthalen-1-ylazo)-nitrobenzene and (B) 2-(2-Hydroxy-naphthalen-1-ylazo)-benzoic acid.

The Freundlich model of isotherm assumes heterogeneous sites having energetically different adsorption sites which are not equally accessible. The Freundlich isotherm can be written as:

$$LnD_f = Lnk_f + \frac{1}{n} LnD_s \qquad (2)$$

where, D_f is the amount of adsorbent at equilibrium (mg/g); D_s, is the adsorbent concentration in solution (mg/dm) at equilibrium; and k_f and n, are the constants which include all factors affecting the adsorption process. With the increase in adsorption capacity of the adsorbent, the k_f value increases for the given adsorbate. The heterogeneity factor is $1/n$ and if n is close to unity, the surface heterogeneity is less important but as the value of n approaches 10, the surface heterogeneity becomes increasingly significant [29].



Product	R	%Yield
2-(2-Hydroxy-naphthalen-1-ylazo)-nitrobenzene	2-NO_2	96
2-(2-Hydroxy-naphthalen-1-ylazo)-benzoic acid	2-CO_2H	91.5

Figure 4: Diazotization of anilines using nano silicagel supported by thionyl chloride as a solid acid and diazo-coupling with 2-naphtole.

Figure **7** shows the plots of ln D_f versus ln D_s for the adsorption of the two synthesized dyes onto wool. k_f and $1/n$ were obtained from the slope and intercept of such a plot (Table **3**).

The linear regression method was used to determine the better fit isotherm in adsorption process. As shown in Tables **2** and **3**, Langmuir isotherm is coinciding well with the experimental data because R^2 is closer to unit. Homogeneous distribution of active positions on wool is a reason of this fact that Langmuir isotherm may be compatible well with experimental data. The applicability of the Langmuir isotherm suggests monolayer coverage of the two synthesized dyes on surfaces of wool fiber.

Conclusion

This research was conducted to introduce an efficient and simple method for the synthesis of azo dyes by conventional method in good yield. It can be implied from the results that using this new method in order for synthesis of the dyes based on β-naphthol is economical and harmless to the environment due to the elimination of dense liquid acids. After synthesis, the dyes were applied to wool fabric, and their sorption properties on the wool fabrics were investigated. The constants obtained from the equations of two Freundlich and Langmuir isotherm equations and the obtained correlation coefficient show that these synthesized dyes have better coinciding with Langmuir isotherm.

Experimental

Materials and instruments:

A 100% wool fabric with twill structure, and 163 g/m^2 fabric mass was used. The chemicals used in this research were purchased from Fluka (Buchs, Switzerland) and were used without further purification. Melting points were determined with an Electrothermal 9100 apparatus. Elemental analyses were performed using a Costech ECS 4010 CHNS-O analyzer. Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu 8400 FTIR spectrophotometer. The UV-Visible spectra were obtained on a Varian Cary 100 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX-500 Avance spectrometer at solution in CDCl3 using TMS as internal standard.

Preparation of nano silicagel supported by thionyl chloride:

Nano silicagel (5 g) with a particle size of 20 nm was placed in oven for 1h in order to activate it. Thionyl chloride (10 mL) was then added gradually over 15 min and the reaction continued for 1h with stirring. The temperature of the mixture was then increased to 70°C. The resulting compound was placed in vacuum desiccator for 24 h to obtain the white powder of nano silicagel supported by thionyl chloride.

General procedure for preparation of dyes:

The supported nano silicagel (0.04 g) was added to a magnetically stirred solution of 2-nitroaniline or 2-aminobenzoic acid (1 mmol) and sodium nitrite (2 mL,10%) in acetone (10 mL). The reaction mixture was then stirred for 10 min at room temperature, while stirring to obtain diazonium salt solution. The resulting diazonium salt was slowly added to the solution of 2-naphtol (1 mmol) in acetone, and sodium hydroxide (5 mL, 5%) was added to adjust the pH to 6-7. The reaction mixture was then stirred for 10 min at room temperature. The solvent was evaporated at reduced pressure. The residue was precipitated, filtered and washed with diethyl ether to obtain the pure product. The characterization data of the synthesized dyes are as follows:

2-(2-Hydroxy-naphthalen-1-ylazo)-nitrobenzene:

Yield: 96%; Scarlet powder; m.p. 279-283°C; UV/Vis (water) λ_{max} =412 nm. IR (KBr)(ν_{max}, cm^{-1}): 3345 (OH), 1567, 1345 (NO$_2$), 1455 (N=N), 1383 (C-N). Analyses: Calcd. For $C_{16}H_{11}N_3O_3$(293 g/mol): C, 65.52; H, 3.78; N, 14.32%. Found: C, 65.39; H, 3.67; N, 14.13%. ^{1}HNMR (500 MHz, CDCl3) δ (ppm): 7.68 (1H, d, J= 7 Hz), 7.62 (1H, d, J= 7 Hz), 7.50 (1H, dd, J= 7 and 2 Hz), 7.44 (1H, dt, J= 7 and 2 Hz), 7.40 (1H, dt, J= 7 and 2 Hz), 8.28 (1H, dd, J= 7 and 2 Hz), 7.63 (2H, d, J= 7), 7.52 (2H, d, J= 7). ^{13}C NMR (125.8 MHz, CDCl3) δ (ppm): 170.04, 169.37, 157.60, 146.98, 137.82, 136.07, 130.62, 128.03, 127.50, 127.03, 125.79, 124.59, 123.70, 119.86, 116.85, 115.78, 108.8.

2-(2-Hydroxy-naphthalen-1-ylazo)-benzoic acid:

Yield: 91.5%; Brown powder; m.p. 148-150°C; UV/Vis (water) λ_{max} =488 nm. IR (KBr)(ν_{max}, cm^{-1}): 3424 (OH), 1693 (C=O, acid), 1588, 1529, 1448. Analyses: Calcd. For $C_{17}H_{12}N_2O_3$(292 g/mol): C, 69.86; H, 4.14; N, 9.58%. Found: C, 69.72; H, 3.96; N, 9.65%. ^{1}HNMR (500 MHz, CDCl3) δ (ppm): 12.18 (2 H, broad s, 2OH), 8.06 (1H, dd, *J*= 7 and 2 Hz), 7.69 (2H, m), 7.54 (1H, d, *J*= 7 Hz), 7.41 (1H, dd, *J*= 7 and 2 Hz), 7.41 (1H, dt, *J*= 7 and 2 Hz), 7.49 (1H, d, *J*= 7 Hz), 7.35 (1H, dt, *J*= 7 and 2 Hz), 7.11 (2H, m). ^{13}C NMR (125.8 MHz, CDCl3) δ (ppm): 172.64, 140.07, 138.24, 135, 37, 133.25, 131.17, 128.90, 128.29, 127.61, 124.50, 121.45, 120.41, 120.13, 119.24, 117.09, 116.46, 110.33.

Table 1: Percent yields of azo compounds synthesized by different sources.

Product name	NaNO$_2$/HCl(aq)	Fe(NO$_3$)$_3$/HCl(aq)	HNO$_3$ (aq)/HCl(aq)	HNO$_3$ (aq)/HCl(g)
(2-(4-nitrophenyl)diazenyl) naphthalene-2-ol	26	47	53	60
1-(2-phenyldiazenyl) naphthalene-2-ol	39	35	60	60

Table 2: Constants acquired from Langmuir isotherm of the two synthesized dyes.

	2-(2-Hydroxy-naphthalen-1-ylazo)-nitrobenzene			2-(2-Hydroxy-naphthalen-1-ylazo)-benzoic acid		
Temperature	*kL*	q_m	R^2	*kL*	q_m	R^2
40°C	12.2307	3.144	0.963	20.9459	1.2903	0.968
50°C	3.2	15.625	0.983	19.7777	1.4044	0.977
60°C	1	55.55	0.985	17.2222	1.6129	0.982
70°C	0.72	76.9230	0.985	10.55	1.3696	0.978
90°C	0.7333	90.9090	0.942	8.6341	2.8248	0.982

Table 3: Constants acquired from Freundlich isotherm of the two synthesized dyes.

	2-(2-Hydroxy-naphthalen-1-ylazo)-nitrobenzene			2-(2-Hydroxy-naphthalen-1-ylazo)-benzoic acid		
Temperature	k_f	*n*	R^2	k_f	*n*	R^2
40°C	269.077	0.7147	0.957	1.5418	3.095	0.787
50°C	167.67	0.7930	0.979	2.4967	2.1929	0.916
60°C	106.8	0.8525	0.978	2.8892	2.061	0.930
70°C	86.86	0.9596	0.937	2.1946	2.6178	0.938
90°C	64.9098	1.020	0.973	5.6519	1.4388	0.969

Dyeing procedure and sorption studies:

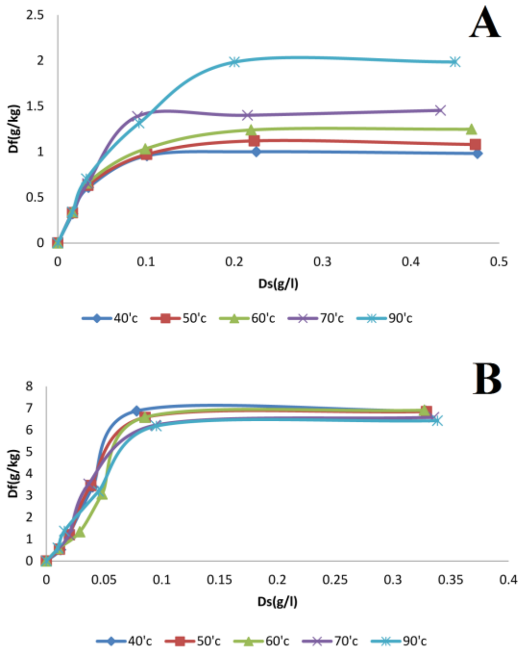


Figure 5: Adsorption isotherm of the synthesis dyes (A) 2-(2-Hydroxy-naphthalen-1-ylazo)-nitrobenzene and (B) 2-(2-Hydroxy-naphthalen-1-ylazo)-benzoic acid.

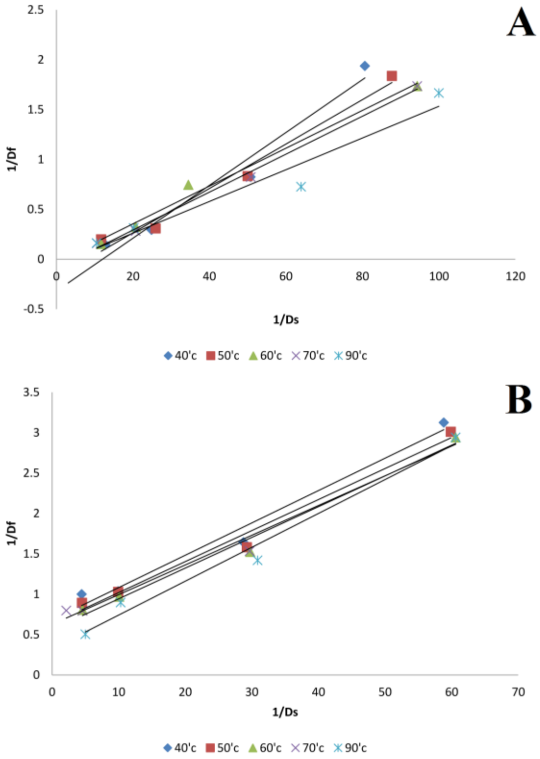


Figure 6: Langmuir adsorption isotherm of 2-(2-Hydroxy-naphthalen-1-ylazo)-nitrobenzene (A) and 2-(2-Hydroxy-naphthalen-1-ylazo)-benzoic acid (B) on wool fabric at different temperatures.

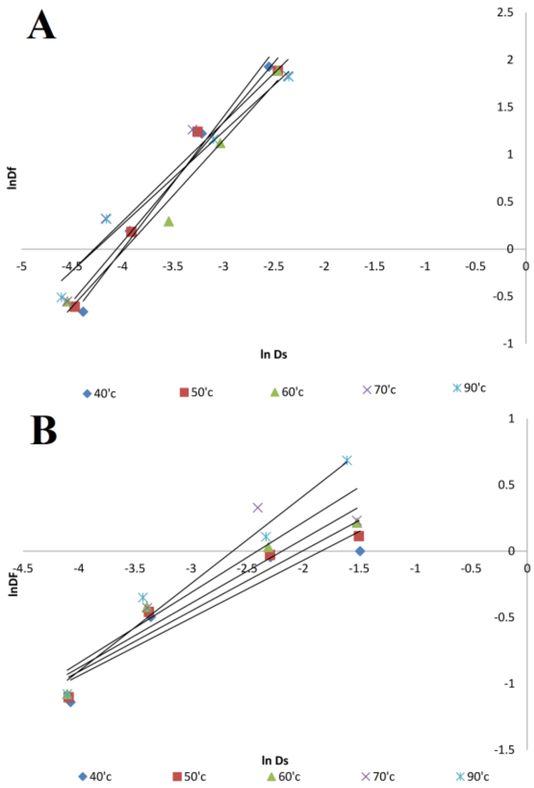


Figure 7: Freundlich adsorption isotherm of 2-(2-Hydroxy-naphthalen-1-ylazo)-nitrobenzene (A) and 2-(2-Hydroxy-naphthalen-1-ylazo)-benzoic acid (B) on wool fabric at different temperatures.

All dyeing procedures were carried out in an AHIBA dyeing system under the following conditions: pH: 5-5.5; temperatures: 40, 50, 60, 70 and 90°C; electrolyte concentrations: 2.5 g/L NaCl; dye concentrations: 0.1, 0.2, 0.5, 1 and 2 percent on weight of fabric (O.W.F); time of dyeing: 2 h (until equilibrium is reached); liquor ratio: 40:1. Dye concentrations were determined for dyeing using spectrophotometry data at the λ_{max} of each dye.

The absorbency of residual dyeing solution was measured with UV-Vis spectrophotometer and the dye concentration of final bath ($[D]_s$, gL^{-1}) was calculated using calibration curve of the synthesis dyes according to Lambert-Beer law. The dye concentration in the fabric at equilibrium ($[D]_f$, g/kg) was obtained with subtraction. Then adsorption isotherm of the synthesis dyes on wool was drawn.

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