



Research article

An eco-friendly methodology for the synthesis of azocoumarin dye using cation exchange resins



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ABSTRACT

An azo dye bearing coumarin moieties were prepared by diazotization of 4-Nitro aniline using amberlyst-15 as an acid catalyst then coupling of the obtained diazonium salt with coumarin. The obtained dye were characterized via UV-Vis, FT-IR, and ^1H , ^{13}C NMR spectroscopy. This *eco-friendly* procedure seeks to get rid of the restrictions of the diazotisation traditional method such as using of strong acids, harmful solvents, modest yields and difficult purification. In addition, the pluses of this procedure include moderate conditions with good conversions, avoidance of harmful acids, simple product isolation process, selective, reduce by-products and purification procedures, recyclability of the catalyst and inexpensive procedures.

1. Introduction

Heterocyclic compounds are found in many natural and synthetic compounds and enter into a huge range of applications and uses, mostly in pharmacological fields, as well as in the chemistry of dyes and colors. Among these compounds, coumarins have occupied an important place in most research and attracted wide interest by researchers due to their biological, clinical and industrial applications.

They are used as additives in food products, perfumes, pharmaceuticals and cosmetics, optical bleaches, fluorescent and lasers dyes [1, 2, 3, 4]. Beside that their important use as heterocyclic coupling components to synthesis azo dyes which consider the widest group of organic dyes due to the number of variations and differences in their chemical composition and their wide industrial applications, Since they can be applied to dye various natural and synthetic fibres also, they can be used for coloring plastics, foods, rubber, drugs, printing inks, paints and cosmetics.

The traditional and general method for the synthesis of azo dyes is usually carried out in two steps: first step the diazotization of aromatic primary amines, followed by second step which is the coupling reaction between diazonium salts and activated aromatic or heterocyclic nucleophilic coupling components.

The formation of diazonium salts in the first step begins by protonation of nitrous acid under strong acidic media at low temperatures (0–5 °C) then the azo coupling in the second step is achieved also at low temperature and in the existence of active nucleophilic coupling

structures. The most negatives of this synthetic procedure are low temperature, use of strong acid–base catalyst, decomposition of aryl diazonium salts at room temperature, small yields, and long reaction times. However, the main negative of such synthetic procedure is its environmental damage. The large and continuous acidic and basic waste generated during it lead to significant damage and pollution to the environment.

Recently, great and tremendous development has been made in the field of polymer chemistry that has become known, since the synthetic organic chemical reactions give by-products which require many procedures to get rid of them and get the final product pure of its traces. Whereas when the polymeric catalyst is applied in the organic process, the byproducts attach and bind to the insoluble polymer and are easily separated from the final product by filtration. The use of these cation exchange resins leads to obtaining the desired product with greater yield, less purification procedures, and less waste and large undesirable pollutants [5, 6, 7, 8, 9, 10, 11, 12, 13]. A literature survey shows a few researches on the application of solid acids as catalyst in the diazotization reactions [14, 15, 16, 17, 18] and there is no method about employing amberlyst-15 to synthesis azo coumarin dyes. So, we here seek and focus our efforts to ensure the possibility of using simple and cheap heterogeneous catalysts. So, we try here to report the synthesis of azo coumarin dyes using amberlyst-15 as a cation exchange resin which resolved the environmental problems, exhibit higher activity, selectivity and it can be separated by filtration, recycling and easy separation and purification of desired compound.

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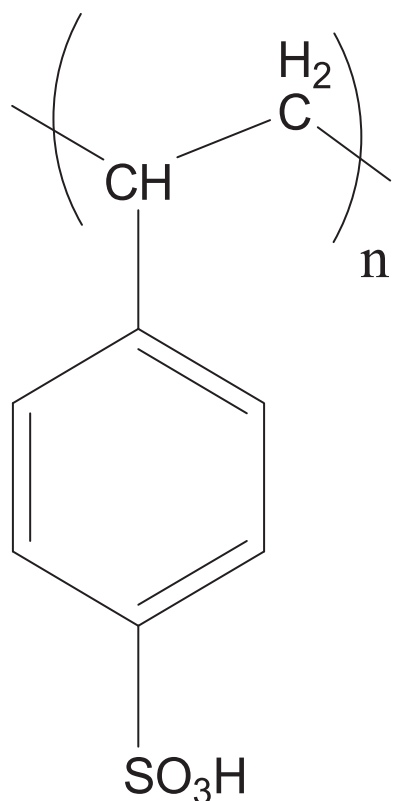


Figure 1. Structure of amberlyst -15.

2. Experimental

2.1. Apparatus

Spectrum NMR proton and carbon device 400 MHz model Bruker by Switzerland company. Optical absorption spectrum infrared device model FT-IR-4100 from the Japanese company Jasco.

2.2. Raw materials and reagents

4-nitro aniline, coumarin (Sigma–Aldrich & Merck), sodium nitrite, sodium hydroxide (99% by Merck), amberlyst-15 (99% by Sigma–Aldrich).

2.3. Experimental procedure

2.3.1. Synthesis of azo coumarin dyes general procedure

To a solution of 4-nitro aniline (1 mmol) in (9 mL) distilled water was added cation-exchange resin (amberlyst-15, 50%), after stirring for 15 min in the ice bath, a solution of NaNO_2 (0.621 g, 9 mmol) in (1.8 mL) distilled water was added gradually during 5 min. The resulting solution was then stirred for 5 min until the starting amine disappeared as monitored by TLC. Then the resulting diazonium salt's solution, was poured from the top of the filter paper to get rid of the catalyst into an ice cold solution of coumarin (0.543 g, 3 mmol) in 20 ml of 10% sodium hydroxide solution, then resulting mixture was stirred and kept on an Ice bath for 30 min at a temperature of 5 °C. The pH was maintained about 6–7. The obtained product was filtered and washed with cold distilled water. Finally, the obtained product was dried and recrystallized by ethanol.

2.4. Characterization of the products

8-[(E)-(4-nitrophenyl)diazenyl]-2H-chromen-2-one orange solid (yield 87%), m.p = 245–247 °C IR(KBr) (ν , cm^{-1}): 1698(C=O), 1350 (C–O), 1610(C=C aromatic), 1480(N=N), 1000(C–N) 1360, 1554 (NO_2) $^1\text{H-NMR}$ (DMSO- d_6 , 400 MHz) (δ , ppm): δ 6.68(d, J = 9.6, 1H, 3-H), 7.67(d, J = 8.9 Hz, 1H, 4-H), 8.29 (d, J = 9.7 Hz, 1H, 5-H), 8.23 (dd, J = 8.9, 2.4, 1H, 6-H), 8.42 (d, J = 2.3, 1H, 7-H), 8.06 (m, 1H, 8-H), 8.13(d, J = 9.2H, 10-H+14-H) 8.49 (d, J = 9.2H, 11-H+13-H), $^{13}\text{C-NMR}$ (DMSO- d_6 , 100 MHz, δ ppm) δ 161.30(C2), 113.33(C3), 144.52(C4), 120.36(C4a), 131.68(C5), 126.35(C6), 126.27(C7), 132.10(C8), 150.30(C8a), 157.39(C9), 121.52(C10+C14), 125.17(C13+C11).

3. Results and discussion

Following up on research in the field of environmentally friendly heterogeneous catalysts, we present the following simple and effective methodology for the synthesis of azo-coumarin dye through the diazotization of aromatic amine in the presence of amberlyst-15 as a heterogeneous and efficient catalyst followed by coupling with coumarins.

Amberlyst-15, which is a brown-gray granules and consists of a reticular polystyrene based on ion exchange resins with strong acidic sulfonic groups (Figure 1). Therefore, it is considered one of the effective heterogeneous acid catalysts in the reactions catalyzed by acidic media. It is safe to use in addition to the possibility of separating it from the reaction mixture easily after the end of the reaction. It is also considered environmentally friendly, especially in terms of the possibility of its renewal and reuses about four times.

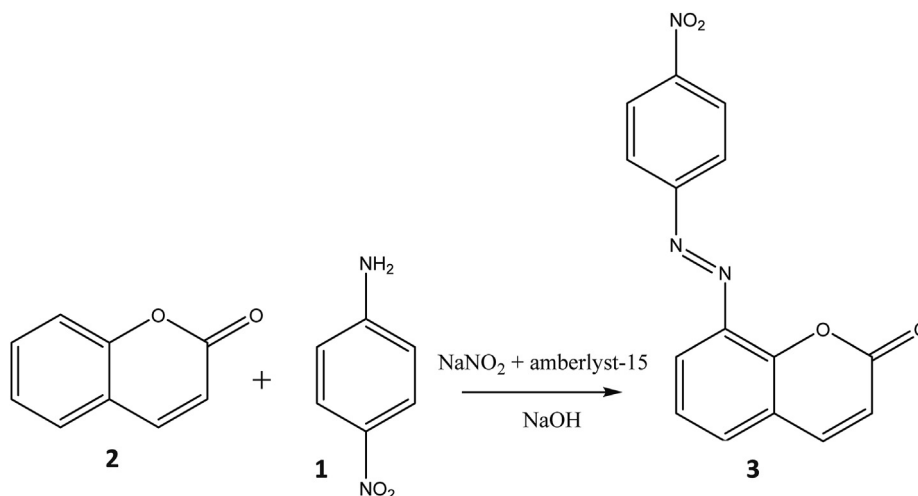


Figure 2. Preparation of dye 3.

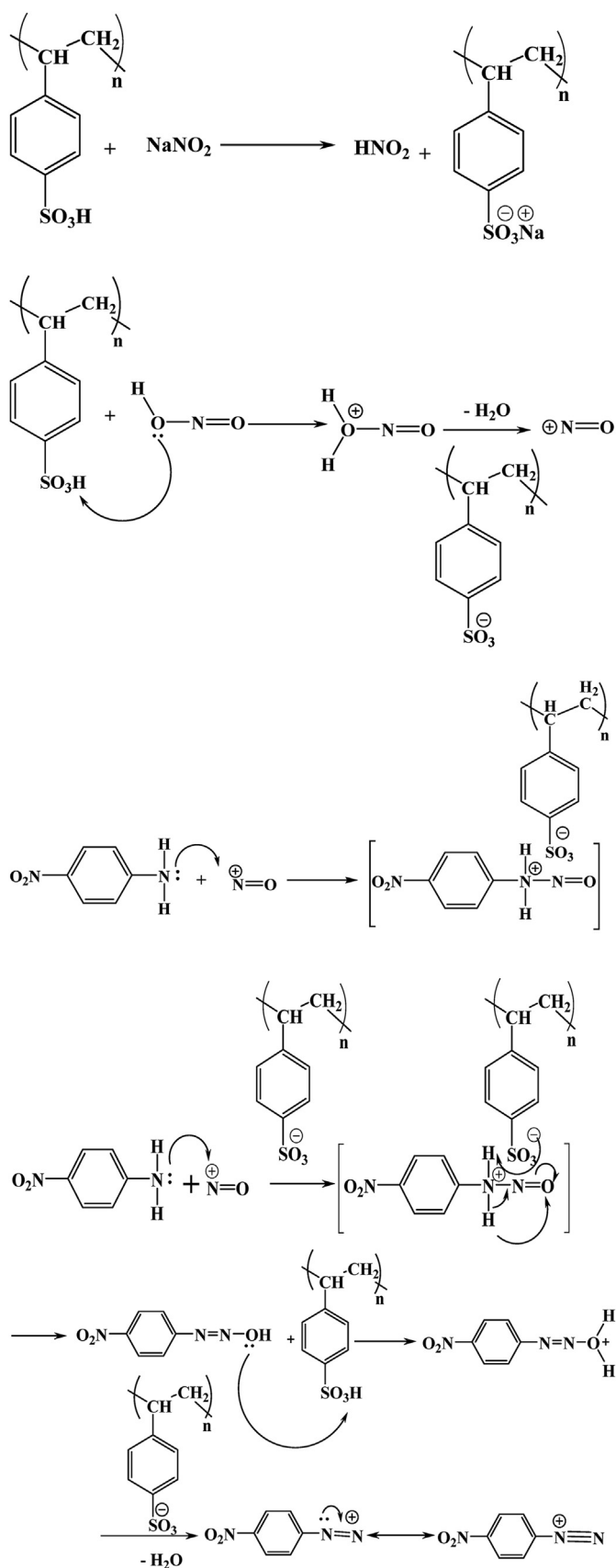


Figure 3. Mechanism of diazotization using amberlyst-15.

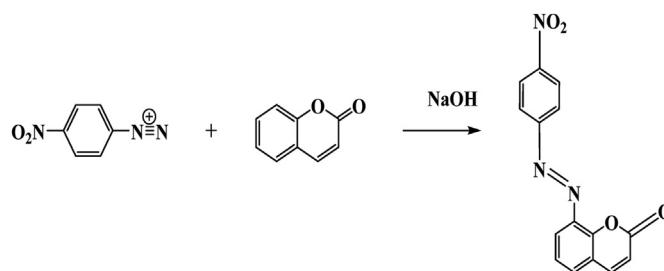


Figure 4. Coupling reaction of diazonium salt with coumarin.

the novel azo coumarin dye **3** were prepared with yield 87% by the diazotization of 4-nitro aniline **1** using amberlyst-15 as catalyst then by coupling with coumarin **2** (Figure 2).

This reaction was carried out firstly according to conventional procedures [12] (The diazotization and diazo coupling reactions are usually performed with protonation of nitrous acid in aqueous media and under strongly acidic conditions) but the reaction mixture showed several byproducts. When this formation of these by products was prevented, and the rate of the reaction was raised beside that the recrystallization was also much easier.

The proposed mechanism for this diazotization in the existence of amberlyst-15 was depicted in Figure 3.

At first, amberlyst-15 was converted to sodium salt to liberate the nitrous acid NaNO_2 . In the next step, the excess of amberlyst-15 contributes to the formation of the nitrosonium ion by removing water from the nitrous acid.

The formation of N-nitroso amine by nucleophilic attack of amino group on nitrosonium ion then elimination of water after series of transfers to produce diazonium salt.

Finally, the nucleophilic attack of coumarin at carbon atom number 8 which have high electronic density [19] forming azo dye (Figure 4).

The main disadvantage of many heterogeneous solid catalysts is that they are damaged and destroyed after work procedures so that they cannot be used later. In our research and these operations, as outlined in Figure 5, the amberlyst-15 showed an important and environmentally friendly advantage in terms of the possibility of recycling it four times and using it in new reactions with a small decrease in its catalytic activity, which It is assumed that it is caused by the partial sedimentation of carbonaceous materials, beside, reduce by-products that was shown in the traditional way by reducing the dissociation of diazonium salts as a result of their binding to the catalyst and thus increased selectivity and increased reaction yields.

The infrared spectra (IR) of the dye **3** (Figure 6) show the following peaks: 1480, 1610 and 1698 cm^{-1} which were assigned the functional groups of, $-\text{N}=\text{N}-$, $-\text{C}=\text{C}$ -aromatic str. and $\text{C}=\text{O}$ str. of α -pyrone of coumarin respectively and The peaks appearing at 1000-1350 cm^{-1} are refer to (C-N) and (C-O) stretching vibration and at 1360 and 1554 cm^{-1} due to the presence of NO_2 str.

The ^1H NMR in $\text{DMSO}-d_6$ spectrum of this dye (Figure 7) exhibited doubled corresponded of two olefinic protons of the coumarin ring (H_3 at 6.60 ppm) and (H_4 at 7.62 ppm), the peaks appearing in the positions 8–8.5 ppm are attributed to aromatic rings protons.

The ^{13}C NMR spectrum of dye **3** (Figure 8) showed 15 distinct peaks in agreement with the dye structure.

The UV-V is electronic absorption spectrum Figure 9 of the dye **3** in dimethyl sulfoxide with a concentration of 0.01% and within the range (350–700 nm) shows a maximum absorption peak at the maximum wavelength 420 nm which is due to the $\pi \rightarrow \pi^*$ transition. We also notice an absorption peak at the wavelength nm 590 and returns to the transition $n \rightarrow \pi^*$ as shown in the Table 1.

This azo coumarin dye can be used as indicators due to the difference in the color of its solution according to the nature of the medium, where it gives a yellowish-orange color in the acidic medium (Figure 10) and a

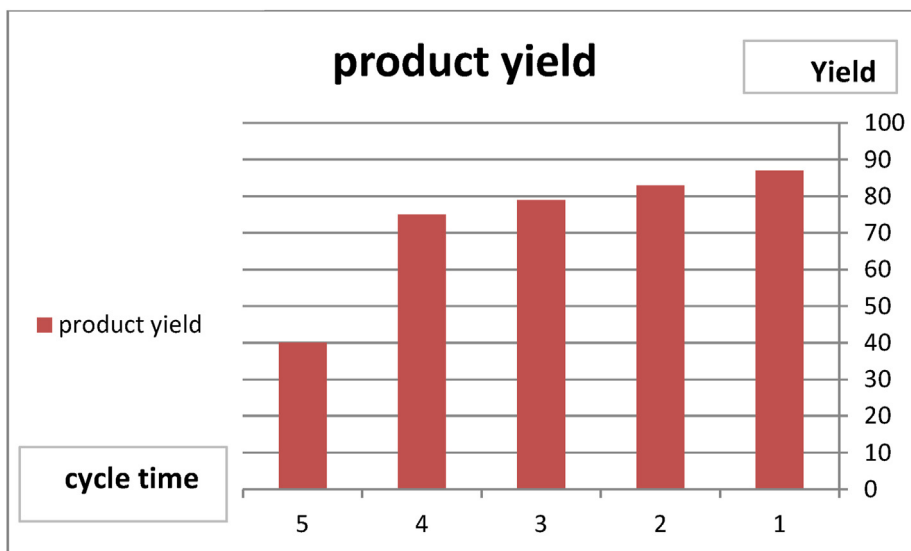


Figure 5. Amberlyst-15 recycle.

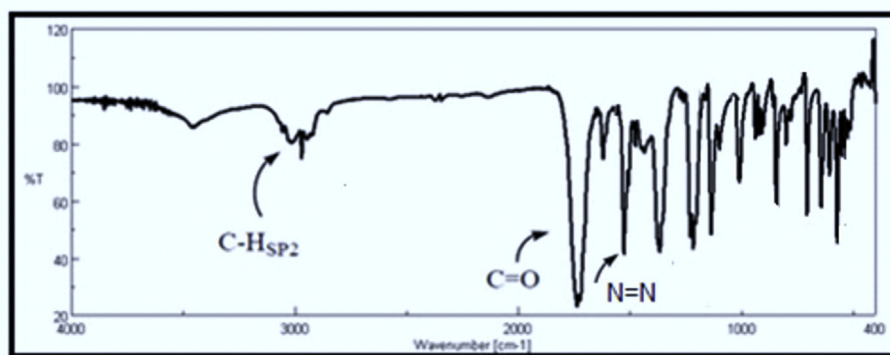


Figure 6. Infrared spectra (IR) of the dye 3.

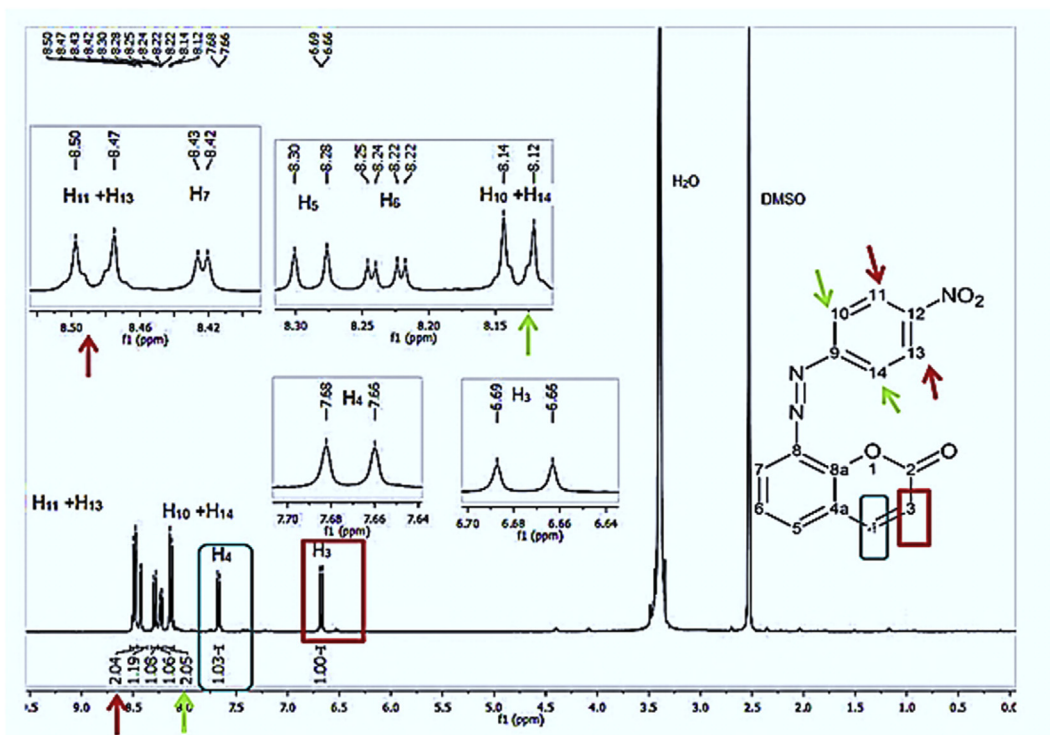


Figure 7. ¹H NMR in DMSO-d₆ spectrum of dye 3.

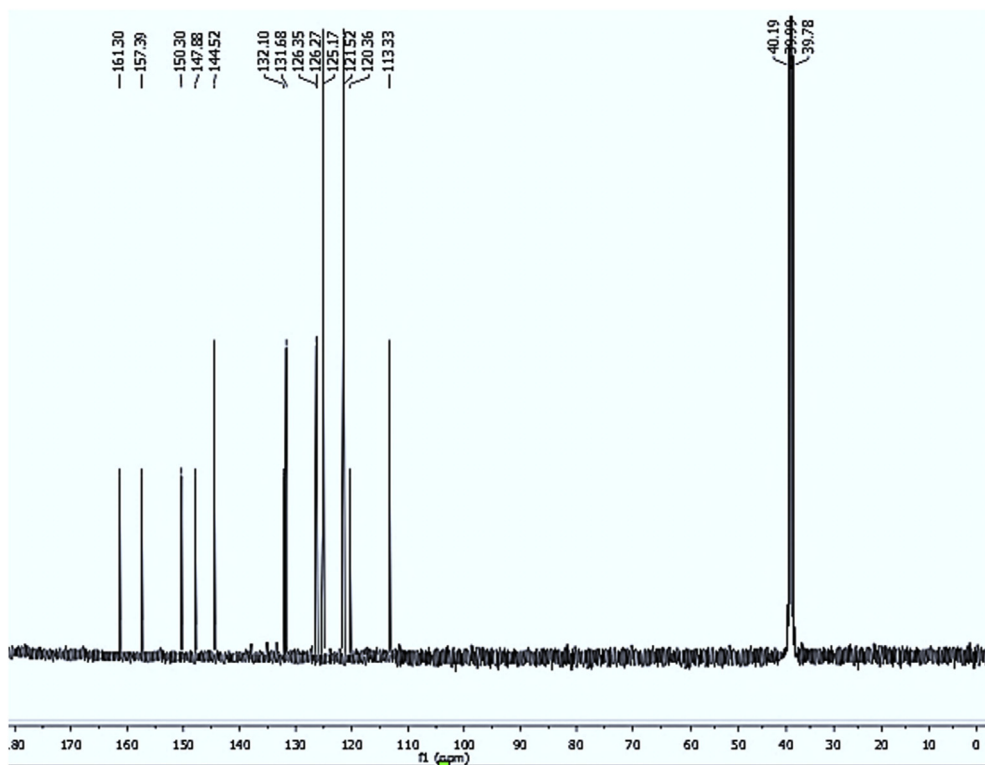


Figure 8. The ^{13}C NMR spectrum of dye 3.

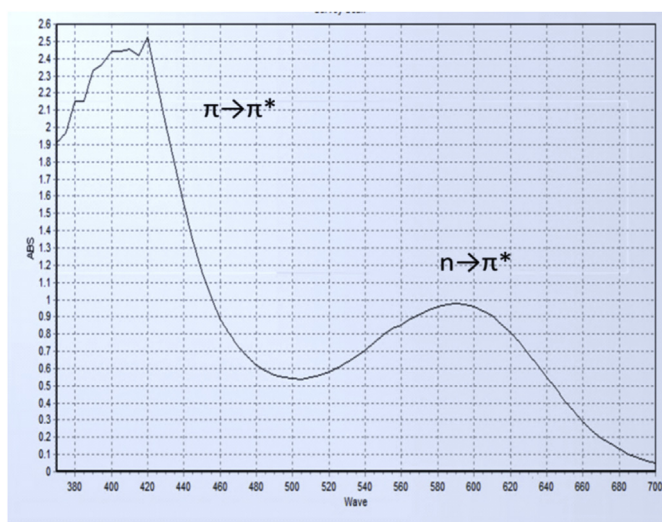


Figure 9. UV-VIS spectrum of dye 3 in DMSO.

purple color in the basic medium (Figure 11), and after preparing various acidic and basic solutions (Figure 12) and following up on the field of color change, which was found to be within the field pH (8.8–11.2).

We think that the cause of this changing in the colour refer to resonance change as shown in Figure 13.

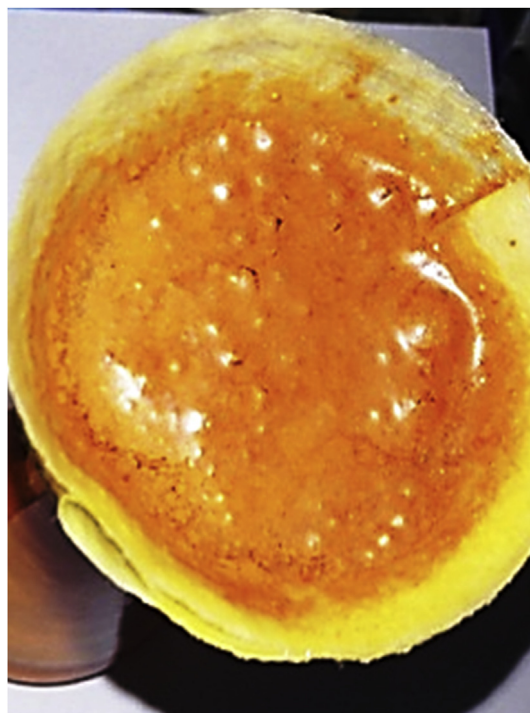


Figure 10. Dye's color in acidic medium.

Table 1. Absorption peaks of dye 3 in the range (350–700 nm).

λ_{max}	Abs	Electron transition
420 nm	2.523	$\pi \rightarrow \pi^*$
590 nm	0.975	$n \rightarrow \pi^*$

4. Conclusions

In summary, we have developed a great method that falls within the field of green chemistry for the synthesis of azo coumarin dyes using amberlyst-15 as a heterogeneous catalyst. Moreover the low cost of the



Figure 11. Dye's color in basic medium.

catalyst comparison with other traditional catalysts such as sulfuric acid

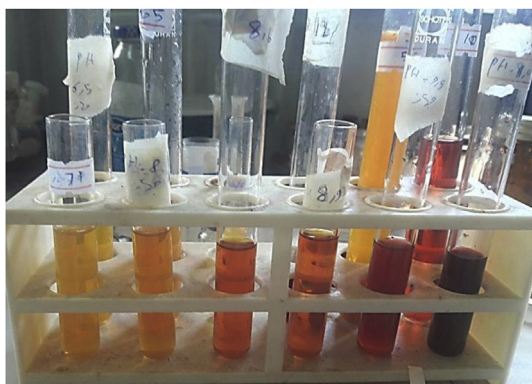


Figure 12. Changing the color of dye's solutions in various pH range.

and hydrochloric acid and by reused four times, low toxicity of the catalyst, simple experimental procedure, and high yields of the products, a novel azo source are the advantages which make this method effective for organic synthesis and convenient and economical to suit the industrial and applied fields.

Declarations

Author contribution statement

Fadia Alhaj Hussien: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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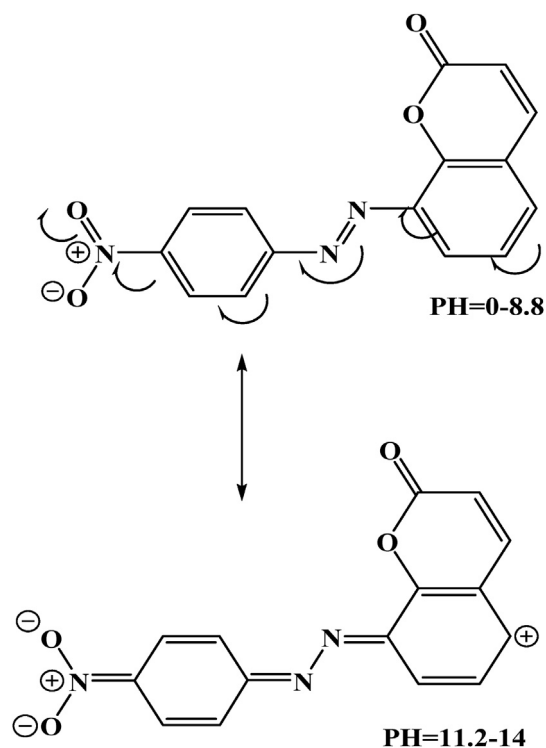


Figure 13. Suggested resonance which causing color change.

Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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References

- [1] O. Kennedy, D.R. Thornes, *Coumarins: Biology, Applications and Mode of Action*, Wiley and Sons, Chichester, 1997.
- [2] M. Zahradnik, *The Production and Application of Fluorescent Brightening Agents*, Wiley and Sons, 1990.
- [3] H.D.R. Murray, J. Mendez, S.A. Brown, *The Natural Coumarins: Occurrence, Chemistry and Biochemistry*, Wiley and Sons, New York, 1982.
- [4] R. Hari Maradiyaa, S. Vithal Patelb, Synthesis and dyeing performance of some novel heterocyclic azo disperse dyes, *J. Braz. Chem. Soc.* 12 (6) (2001) 710–714.
- [5] A. Corma, H. Garcia, Silica-bound homogenous catalysts as recoverable and reusable catalysts in organic synthesis, *Adv. Synth. Catal.* 348 (2006) 1391–1412.
- [6] M.J. Astle, in: C. Calman, T.R.E. Kressman (Eds.), *Ion 'Exchangers in Organic and Biochemistry'*, Interscience, New York, 1957, p. 658. Chapter 36.
- [7] R.B. Merrifield, Solid phase peptide synthesis. I. The synthesis of a tetrapeptide, *J. Am. Chem. Soc.* 85 (1963) 2149.
- [8] R.L. Letsinger, M.J. Kornet, Popcorn polymer as a support in multistep synthesis, *J. Am. Chem. Soc.* 85 (1963) 3045.
- [9] N.K. Mathur, C.K. Narang, R.E. Williams (Eds.), *Polymers as Aids in Organic Chemistry*, Academic Press, New York, 1980.
- [10] P. Hodge, D.C. Sherrington (Eds.), *Polymer Supported Reactions in Organic Synthesis*, Wiley, Chichester, 1980.

- [11] P. Sudhir Kumar, J. Sahoo, Evaluation of in-vitro antimicrobial activity of some newly synthesized 7-hydroxy 4-methyl coumarin congeners, *Der Pharm. Lett.* 7 (2) (2015) 60–64.
- [12] E. Merino, Synthesis of azobenzenes: the coloured pieces of molecular materials, *Chem. Soc. Rev.* 40 (2011) 3835–3853.
- [13] M.S. Bashandy, F.A. Mohamed, M.M. El-Molla, M.B. Sheier1, A.H. Bedair, Synthesis of novel acid dyes with coumarin moiety and their utilization for dyeing wool and silk fabrics, *Open J. Med. Chem.* 6 (2016) 18–35.
- [14] B. Damodaran, J. Litka, L. Malathy, Modified clays as efficient acid–base catalyst systems for diazotization and diazocoupling reactions, *Synth. Commun.* 33 (6) (2003) 863–869.
- [15] Javad Safari, Zohre Zarnegar, An environmentally friendly approach to the green synthesis of azo dyes in the presence of magnetic solid acid catalysts, *RSC Adv.* 5 (2015) 17738, and Iodination o.
- [16] E.A. Krasnokutskaya, N.I. Semenischeva, V.D. Filimonov, P. Knochel, A New, One-step, Effective Protocol for the Iodination of Aromatic and Heterocyclic Compounds via Aprotic Diazotization of Amines, Thieme Stuttgart, New York, 2007, pp. 81–84. *SYNTHESIS*, No. 1; x.x.2006.
- [17] V.D. Filimonov, M. Trusova, P. Postnikov, E.A. Krasnokutskaya, Y. Min Lee, H.Y. Hwang, H. Kim, Ki-Whan Chi, Unusually stable, versatile, and pure arenediazonium tosylates: their preparation, structures, and synthetic applicability, *Org. Lett.* 10 (18) (2008) 3961–3964. Diazotization and iodination.
- [18] F.M. Akwi, P. Watts, The in situ generation and reactive quench of diazonium compounds in the synthesis of azo compounds in microreactors, *Beilstein J. Org. Chem.* 12 (2016) 1987–2004.
- [19] P.S. Song, W.H. Gordon, Spectroscopic study of the excited states of coumarin, *J. Phys. Chem.* 74 (24) (1970) 4234.