

Intercalation of xylenol orange, morin and calmagite into NaY zeolite and their application in dye/zeolite modified electrode

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Abstract The intercalation of xylenol orange, morin and Calmagite into NaY zeolite were studied by XRD, TGA, and BET and diffuse reflectance. These dye incorporated into NaY zeolite by ion exchange in aqueous phase. Results show that xylenol orange can be intercalating better into zeolite. The dye molecules are strongly retained in the channels of zeolites. The prepared intercalated dye/zeolite, for the first time, was used as the modifier for carbon paste electrode. The dye/zeolite modified carbon paste electrode was developed for the voltammetric determination of Cu(II). Copper(II) was selectively preconcentrated. Results shows the peak current intensity increased in order of calmagite > xylenol orange > morin dyes intercalated in zeolite. The results agree with complex formation of those dyes as chelating agents with Copper(II).

Keywords Intercalation of dye · Zeolite · ZME · Copper(II)

Introduction

The structural properties of zeolite, i.e. defined cages and channels of uniform sizes, are ideal for obtaining highly organized arrangements for a large variety of organic dye molecules. A crucial property of zeolite application of dye loaded zeolite as pigments is stability against solvents and thermal stability [1].

Recently, several different applications have been described for zeolite—host dyes, e.g., in the optical second

harmonic generation [2], in photochemistry and in photochemical and physical whole burning. Another promising field of interest with potential for industrial application is the use of dye loaded zeolite as pigments. There are several reports of encapsulation of organic dyes in micro porous materials by ion exchange of cationic dyes, vapor phase deposition ship in the bottle synthesis or addition to hydrothermal synthesis and vapor phase deposition [3–5].

The method to be used depends on the charge, stability and solubility of the guest molecules. Cationic guest molecules such as methylene blue can be incorporated via ion exchange [6].

The attractive properties of zeolite, such as ion exchange capacity, shape and charge selectivity, high thermal stability, low cost and resistance to extreme chemical conditions, extend their applications catalyst adsorbents, sensors and in other advanced materials including zeolite modified electrode (ZME). ZMEs became popular in the mid-1980s and received great interest from the electrochemists during the last decade. Hence, ZMEs have been used in various inorganic, organic and metallic cation analysis [7, 8]. Applications of ZMES are generally based on the ion exchange and electron transport mechanisms by using synthetic zeolite molecular sieves [9].

Modified electrodes offer unique well recognized advantages prepared by immobilizing the chemical species. There is a report on electrochemical behavior of methylene blue immobilized in mordenite and use of this matrix for preparation of a carbon paste electrode to study electrocatalytic oxidation of ascorbic acid [10].

In this work, for the first time we report incorporation of dye (xylenol orange, morin and calmagite) into NaY zeolite ion exchange method. We have chosen NaY zeolite because its structure has Si/Al ratio about 1–5.6 that a strong acid zeolite with the internal voids of zeolite Y are

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formed by almost spherical cages (12A° of diameter) tetrahedrally interconnected through smaller windows (7.4A° of diameter) defined by 12 oxygen rings. This dimension is close to the Van der Waals radii of dyes. It seems that some of dye molecule can be incorporated into NaY zeolite because it has a flexible structure [10]. In the second part, a new carbon paste electrode modified with NaY/dyes zeolite was prepared for determination of Copper(II) by using differential pulse cathodic stripping voltammeter method.

Experimental

Sample preparation

All the reagents were obtained from Merck and used as they received. NaY zeolite was prepared by a hydrothermal synthesis method as previously reported [11]. The dye loaded into the synthesized NaY zeolite by following method:

About 2 g of the NaY sample was stirred in 100 mL of 10^{-5} M aqueous solution of dye (xylenol orange, morin and calmagite) for 24 h at room temperature, pH of solution fixed at 9 by use of NH_4Cl and NH_3 buffer solution. Then the solution was decanted and the solid was dried at 100 °C for 5 h. The dye loaded samples were extracted with ethanol. The extraction step was continued until the solvent became colorless.

Apparatus

The crystallinity of samples was checked by X-ray diffractometer (Philips 8440) with radiation at room temperature $\text{Cu-K}\alpha$. Diffuse reflectance spectra were recorded by a UV–2100 Shimadzu Spectrophotometer equipped with an integrating sphere assembly. A special cell loaded with solid sample was used in all measurements. The spectra were recorded against Barium sulfate at room temperature and plotted in terms of absorbance. TGA and DSC were recorded by a rheometric scientific STA-1500 with speed 10 °C per 1 min.

Electrode preparation and electrochemical measurement

100 mg of zeolite NaY or zeolite NaY modified with intercalated xylenol orange, calmagite or morin dyes was thoroughly mixed with 600 mg carbon powder individually in a mortar. Subsequently, 300 mg mineral oil was added and mixing was continued until a homogeneous paste was obtained.

For electrode fabrication, the prepared paste was packed into one end of a glass tube (approximately 3 mm bore?) and a copper wire was inserted into the other end to make electrical

contact. A fresh electrode surface can be rapidly generated by extruding a small plug of the paste by pushing with copper rod, scraping off the excess and smoothing on a piece of stiff, white paper until a shiny, smooth surface is obtained.

For electrochemical measurements the zeolite modified carbon paste electrode (ZMCPE) was immersed in 50 mL, 5×10^{-5} M Copper(II) nitrate solution & 0.05M sodium nitrate electrolyte solution for 15 minutes, at open circuit. Subsequently the electrode was removed from solution & thoroughly washed with triply distilled water & then plunged in 50 mL, 0.05 M sodium nitrate solution & voltammograms were obtained. The voltammograms were recorded by negative going differential pulse scan 0.3t-0.2V.

Differential pulse voltammograms were obtained using an Autolab PGSTAT 30 potentiostat Galvanostat. The electrochemical cell was constructed with a carbon paste electrode modified with intercalated xylenol orange, morin or calmagite into NaY zeolite as the working electrode, a platinum wire as the auxiliary electrode & saturated calomel electrode as the reference electrode.

Differential pulse voltammetry experiments were carried out with pulse amplitude of 50 mV, a scan rate of 20 mV s⁻¹ and a pulse interval of 0.3 s.

Result and discussion

X-ray diffraction

Figure 1 shows XRD pattern of a mixture of xylenol orange, morin and calmagite onto NaY after ion exchange. The d values of pure NaY zeolite are 14.3, 8.75, 7.45, 5.71, 4.98, 3.73, 3.49, 3.15, 3.01 and 2.90. Generally it has been accepted that the absence of X-ray diffraction peaks of a compound in a mixture is due to the fact that the minor component is not detected when present in a very small quantity. However, in a mixture with significant fraction of component, if the minor component is not found to form a stoichiometric compound with the support or dissolution in the support to form a solid solution, the disappearance of peaks is assumed to be due to dispersion of minor component on the surface of support in the form of a monolayer [12]. The disappearance of the XRD peaks of dye crystals in the sample might be also explained by high dispersion of dyes into the channels of NaY zeolite, where the dye no longer exists in the crystalline state.

Thermal analysis

For clarification of status of dispersed dye on the NaY zeolite, thermal behavior of pure zeolite and all samples after ion exchange treatment have been investigated. The

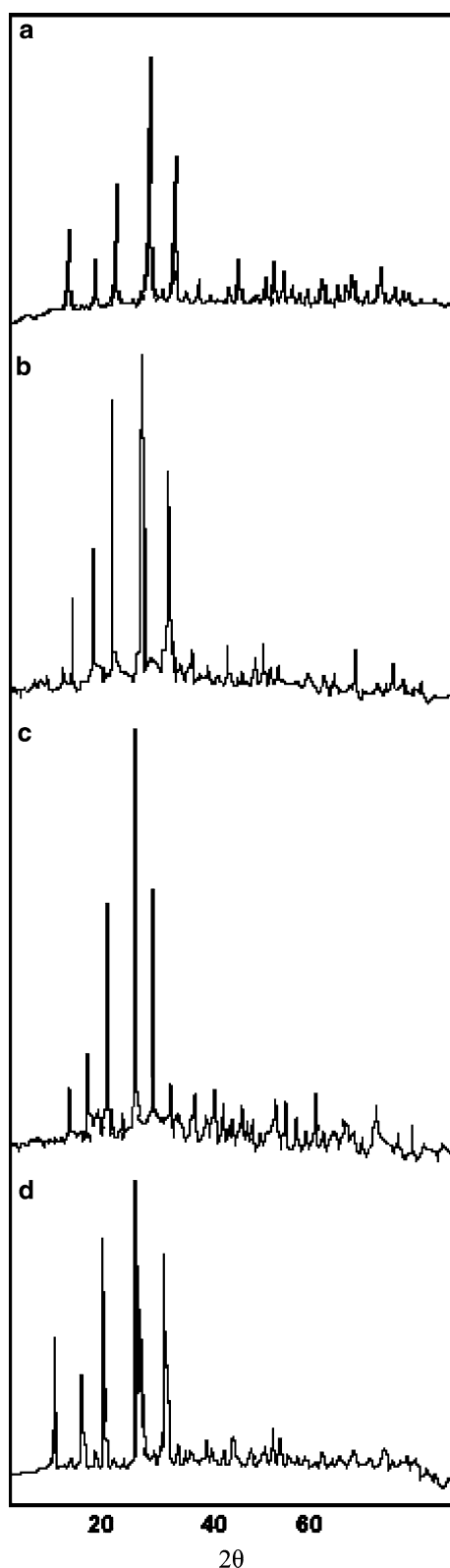


Fig. 1 XRD pattern for (a) NaY (b) Xylenol orange/NaY (c) calmagite/NaY (d) morin /NaY

DTA and TGA curves of NaY zeolite have a typical behavior for this compound. The endothermic peaks at 110 and 150 °C in DTA curve are assigned to desorption of physical and chemical water in NaY. The TGA curve of xylenol orange/Y zeolite shows about 13.2% weight loss upon heating to 200 °C. This weight loss is accompanied by a broad endothermic peak in the DSC curve in the same temperature range, suggesting that the weight loss is due primarily to the elimination of physically adsorbed and possibly chemically bonded water and alcohol. Hence, the second weight loss about 5.55% upon heating to 630 °C related to elimination or decomposed of xylenol orange (Fig. 2a). The weight loss in 200–630 °C about 4.244% and 4.12% for morin and calmagite have been seen, respectively (Fig. 2b, c). The higher percentage for xylenol orange can be related to higher molecular weight of it.

DR spectroscopy

Figure 3 shows the UV-Vis diffuse reflectance spectra of dyes that ion exchange onto zeolite. The spectrum (a) was obtained for xylenol orange onto zeolite, this spectra consist a main band at about 574 nm assigned to the xylenol orange. The band is broadened and the are blue shifted as compared to xylenol orange in aqueous solution (584 nm). The host-guest interaction might be responsible for the blue shift of the absorption bands that is often observed for dyes on mineral carries [13, 14]. The spectra of calmagite onto zeolite shows in Fig. 3b that has a band 565 nm related to calmagite, this band shifted related to aqueous solution at 588 nm. The DR spectrum of morin/zeolite is shown in Fig. 3c. The 397 nm band assigned to morin that a blue shift related to band 415 nm in the aqueous solution of it. The UV-Vis spectra of the encapsulated dyes (xylenol orange, morin and calmagite) onto zeolite show in these material dyes molecules incorporated with zeolite.

Surface area measurements

Table 1 shows the surface area measurement results of NaY zeolite, xylenol orange, morin and calmagite after ion exchange onto zeolite. In contrast to the high surface area of NaY zeolite, 933 m²/g, the surface area of dyes/zeolite after ion exchanged of dye was reduced significantly. This is a further evidence for the dispersion of dyes in pores of NaY zeolite. It is interesting to note that the surface area of xylenol orange/NaY is the lowest among the various samples. It seems that the higher concentration of dyes in pores and channels of xylenol orange/NaY is the reason for

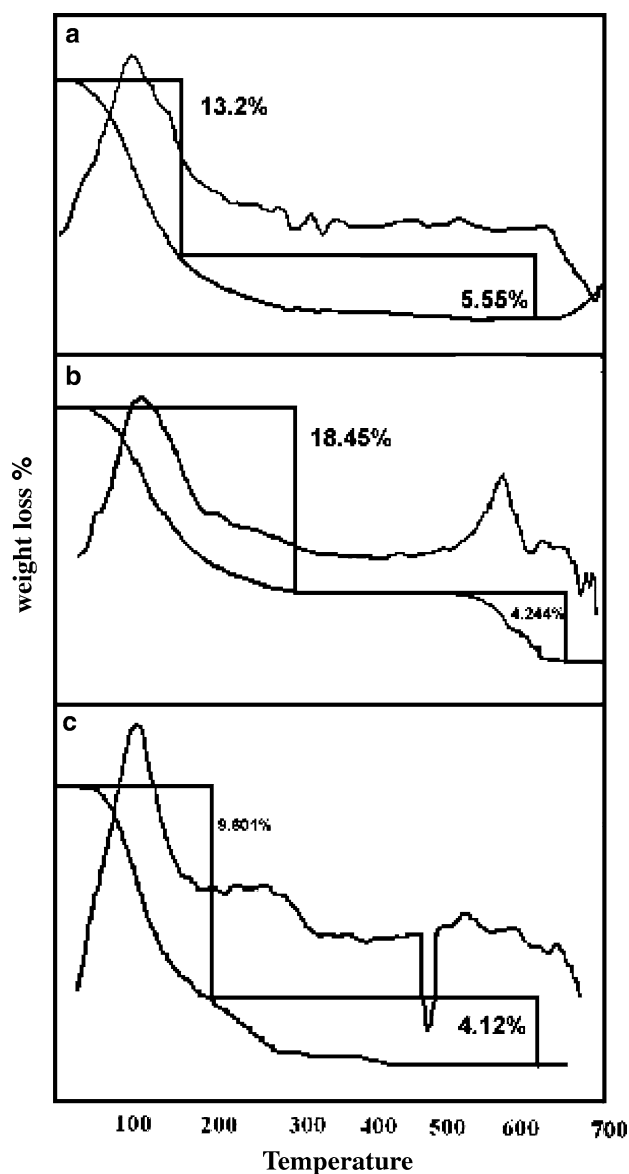


Fig. 2 DTA/TGA curves for (a), xylenol orange/NaY (b) calmagite/NaY (c) morin/NaY

lower surface area of it. It seems that the xylenol orange with ionic form has a good interaction with zeolite and concentration of it higher in zeolite.

Electrochemical measurement

Figure 4 display voltammograms of 5×10^{-5} M, Cu(II) at carbon paste electrode modified with encapsulated calmagite, xylenol orange, morin or pure NaY zeolite. The peak current for reduction of Cu(II) were obtained at 16.4, 15.2, 8.6 and 3.75 mA, respectively. The lowest peak current was observed for carbon paste electrode modified with pure NaY

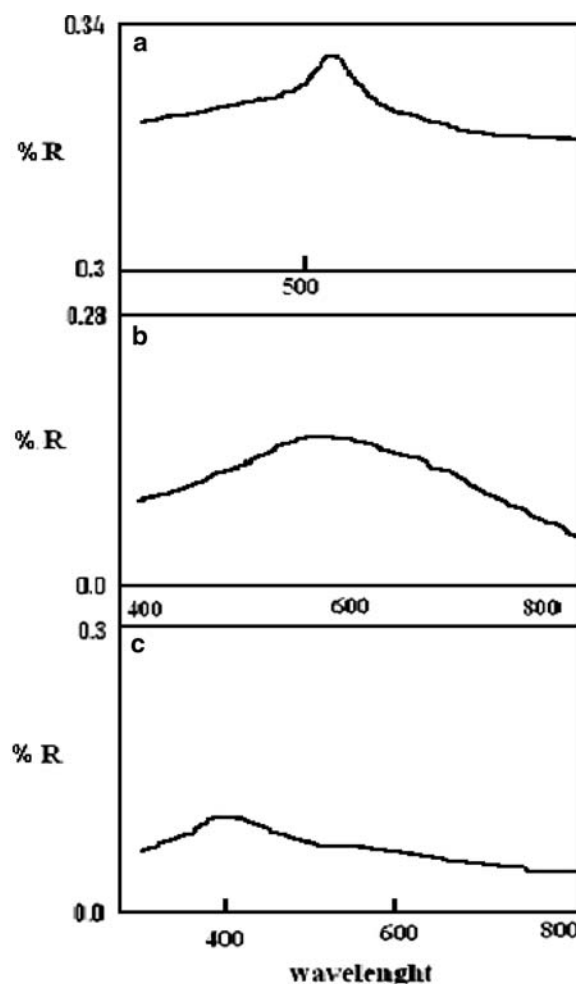


Fig. 3 DRS for (a), xylenol orange/NaY (b) calmagite/NaY (c) morin/NaY

Table 1 Surface area for some dye/NaY after ion exchange (m^2/g)

	NaY	Xylenol orange/ NaY	Calmagite/ NaY	Morin/ NaY
Surface area	933	850	890	915

zeolite. However, higher peak current for carbon paste electrode which is modified with dyes. This means the dyes play as chelating agent for Cu(II), and they assist accumulation of Cu^{2+} in zeolite structure. It seems there is a good relation between complex formation of dyes Cu(II) and peak current. The K_f for calmagite & xylenol orange & Cu(II) 1.07×10^{21} & 3.16×10^{18} were reported [15].

There is another report that reveals morin and Cu(II) has weak complex [16]. The zeolites themselves are not selective to absorption in their holes. However, these results show that we can modify selectivity of zeolite by encapsulation of appropriate dyes as chelating agents by

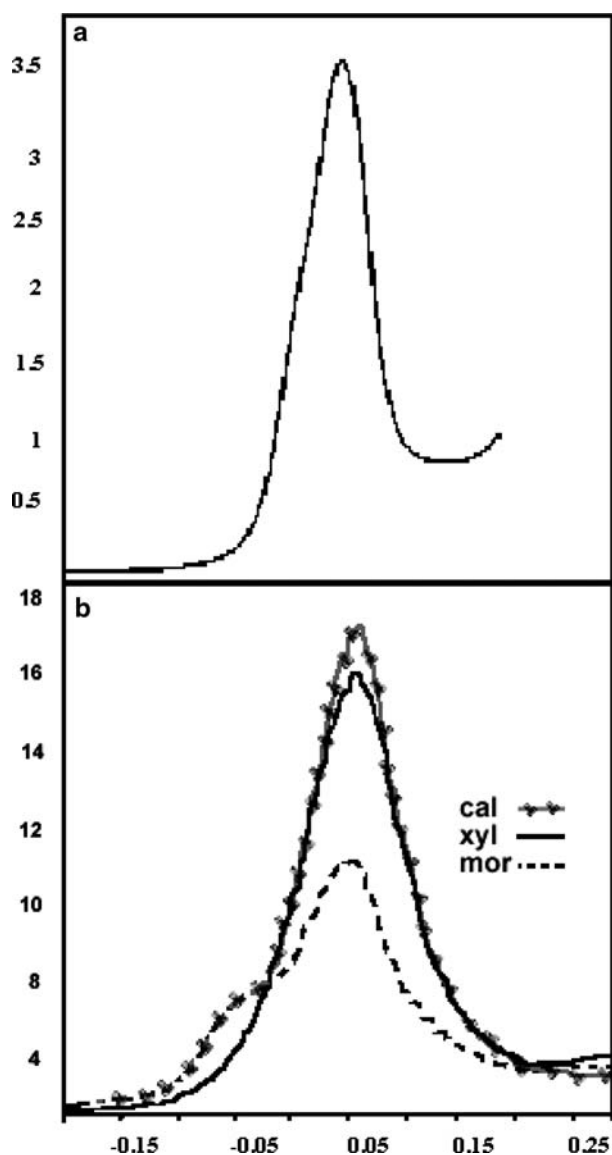


Fig. 4 Display voltammograms of 5×10^{-5} M, Cu(II) at carbon paste electrode modified with pure NaY zeolite (a) encapsulated calmagite, xylenol orange, morin (b)

simple ion exchange method. Our initial experiments revealed that the chemically modified carbon paste electrode (CMCPE) shows stable response up to 3 hours in solution. However, zeolite modified carbon paste electrode (ZMCPE) shows stable response up to 3 days. The carbon paste electrode which modify by direct additions of chemicals (CMCPE) shows lower operational stability due to eventual leaching of chemical from electrode surface which limit their usefulness. Though the proposed ZMCPE shows more stability in CPE due to interaction of chemicals with zeolite which prevent their leakage to the solution. This might be promising area for future analytical studies with ZMCPEs with various ligands to selectively measure several ions.

Conclusion

This paper demonstrates that it is possible intercalated xylenol orange, morin and calmagite into NaY zeolite. Diffuse reflectance spectroscopic, XRD, TGA and BET confirm intercalation of the dyes in zeolite NaY. However, xylenol orange with ionic form shows a good interaction with zeolite and higher concentration in zeolite. These dye/zeolite modified carbon paste electrode was developed for the voltammetry determination of Cu(II). Copper(II) was selectively preconcentrated. Results shows the peak current intensity increased in order of calmagite > xylenol orange > morin modified zeolite in CPE that agrees with complex formation constants of those reagents with Cu(II). The electrochemical results propose a promising area for analytical application of ZMCPEs in future.

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