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Green synthesis and properties of nickel terephthalate complex with 2,2′-bipyridine

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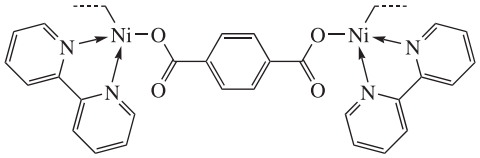
Green synthesis of nickel terephthalate complex with 2,2′-bipyridine involves the preparation of intermediate nickel terephthalate followed by complexation with 2,2′-bipyridine. The resulting substance was tested as an adsorbent for solid-phase extraction of technogenic pollutants.



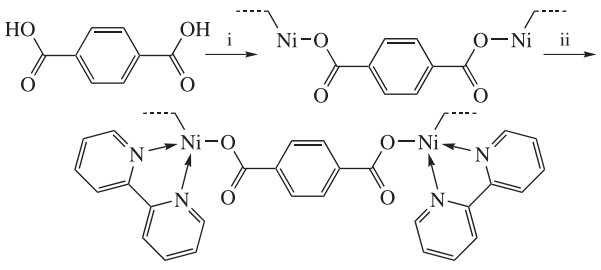
Keywords: metal-organic frameworks, nickel complexes, terephthalates, green chemistry, solid-phase extraction, technogenic pollutants, organic dyes.

In recent decades, science has increasingly focused on the study of metal complexes that form metal-organic frameworks (MOFs).[1,2] Such attention is explained by the remarkable structure of these compounds, their physical and chemical properties. Of particular interest is their use in analytical chemistry for the analysis of food products,[3–5] wastewater treatment,[6] chromatographic separation,[7–9] during sample preparation, in particular, for solid-phase extraction of organic dyes.[10–17] Solid-phase extraction for sample pretreatment offers many advantages, including fast separation, high enrichment and recovery efficiency, low cost, low solvent consumption, no emulsion formation, short processing times, and the opportunity to be combined with various advanced detection methods. Of particular interest are systems in which, in addition to the organic linker, nitrogen-containing heterocyclic systems are present, which are metal-coordinating centers.[18,19] One of the important examples of such ligands is terephthalate ion, since the functional groups in the *para*-position make it possible to obtain polymer chains, forming both monometallic and heterometallic two- or three-dimensional coordination polymers. Based on the possibilities of the structure of the terephthalate ion, it can act as a bi-, tri-, or tetradentate ligand.[18] One of the urgent tasks of studying such compounds is the development of effective methods for their synthesis that satisfy the principles of green chemistry.[20]

The aim of our research was to search for green synthetic methods that are convenient to use and cause minimal damage to the environment. As a rule, syntheses of such compounds are carried out under prolonged heating associated with significant energy costs and the use of hazardous solvents, *e.g.*, DMF, benzene.[21] To obtain MOF, we employed a two-stage procedure with the isolation of intermediate nickel terephthalate followed by its complexation with 2,2′-bipyridine (Scheme 1, for synthetic details see Online Supplementary Materials).

The obtained nickel terephthalate was identified by elemental analysis, IR spectroscopy, and X-ray diffraction (XRD). All the diffraction peaks can be readily indexed to the triclinic phase of basic nickel terephthalate (JCPDS card file no. 35-1677),[22–24] indicating the existence of Ni MOF structure, however there are several peaks that indicate slight contamination of the target product. In addition, of the product obtained possesses the same morphology. Scanning electron microscopy (SEM) image of the compound shows the presence of crystals in the form of rectangular pyramids up to 100×30×10 nm in size [Figure 1(*a*)].

The complexation of nickel terephthalate with 2,2′-bipyridine was carried out in ethanol (see Scheme 1). The product was identified using elemental analysis, IR spectroscopy, and XRD analysis, which were in satisfactory agreement with previously published data.[21] The complexation caused change in the morphology of the product, which acquired a layered structure [Figure 1(*b*)] with dimensions of individual blocks 200×200 nm and insignificant thickness.



Scheme 1 *Reagents and conditions*: i, $NiCl_2·6H_2O$, NaOH, H_2O, 85→20 °C; ii, 2,2′-bipyridine, EtOH, room temperature.

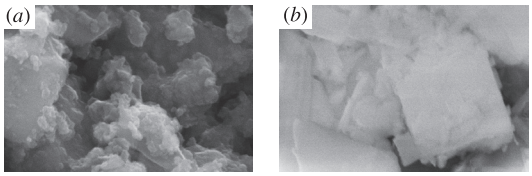


Figure 1 SEM images of (*a*) nickel terephthalate and (*b*) nickel terephthalate complex with bipyridine.

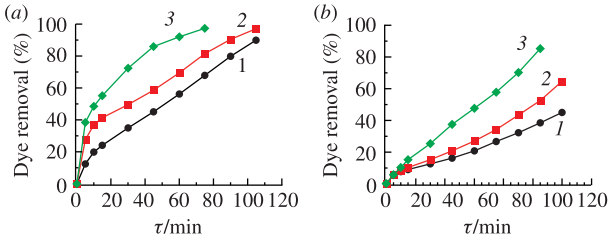


Figure 2 The removal of organic dyes (*a*) Congo red and (*b*) methylene blue *versus* time at temperatures (*1*) 283, (*2*) 292 and (*3*) 308 K.

In accordance with the data of studying the sorption–desorption of nitrogen at 77 K, the surface area of the sorbent is 611.3 m^2 g^{-1} and it changes insignificantly in the course of the experiments.

The resulting complex was investigated for the possibility of its use as a reagent for solid-phase extraction of technogenic pollutants. We chose organic dyes, Congo red and methylene blue, as model pollutant compounds. The experiment, data processing and interpretation were carried out according to the published procedure.[25] Based on the data obtained, we determined the degree of removal of an organic dye from an aqueous solution, which serves as a criterion for the effectiveness of this sorbent, and found that it exhibits a fairly good activity with respect to anionic dyes and satisfactory activity with respect to cationic dyes. It should be noted that the kinetics of sorption in the case of Congo red exceeds that for methylene blue (Figure 2). The limiting adsorption is 121 mg g^{-1}.

The well-known Langmuir isotherm equation[26] was used to interpret the obtained data on adsorption. The Langmuir adsorption isotherms of the studied organic dyes by MOF are shown in Figures 3 and 4.

Table 1 gives the parameters of the Langmuir isotherms of dye adsorption on MOF, the equilibrium rate constant of pseudo-first order adsorption, and the thermodynamic parameters of adsorption. An analysis of the results obtained shows good agreement between the Langmuir model and experimental data (most of the R^2 values exceed 0.9). The separation factor (R_L) values at various temperatures were less than 1 and greater than zero, which indicates favorable adsorption and an increase in the

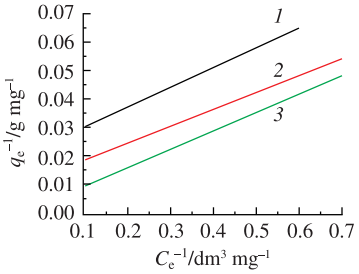


Figure 3 Langmuir isotherms for the adsorption of Congo red at temperatures (*1*) 283, (*2*) 292 and (*3*) 308 K.

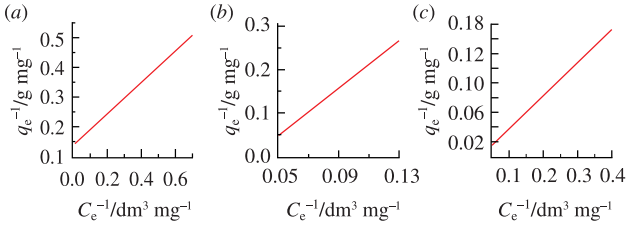


Figure 4 Langmuir isotherms for the adsorption of methylene blue at temperatures (*a*) 283, (*b*) 292 and (*c*) 308 K.

adsorption of dyes with the temperature growth. Least squares regression analysis confirmed the applicability of the pseudo first order kinetic model to the adsorption of dyes using MOF. Negative values of ΔG^o at temperatures of 283, 292 and 308 K indicate a spontaneous adsorption process. A decrease in this parameter with increasing temperature is indicative of an increase in effective adsorption at a higher temperature. A negative value of ΔH^o confirms the exothermal character of the adsorption and indicates a weak interaction between the complex and the dye. A positive value of ΔS^o means an increase in the degree of freedom at the solid–liquid interface during the adsorption of dyes on the complex and the presence of some structural changes in the adsorbent.

In conclusion, MOF based on a complex of nickel terephthalate with 2,2′-bipyridine was successfully obtained by the green method using water and ethanol as solvents. The resulting substance does not require lengthy and expensive washing and long-term drying. A preliminary assessment of the use of the obtained MOF as a sorbent for solid-phase extraction of organic dyes shows that this material has high sorption efficiency, reaching the limiting adsorption of 121 mg g^{-1}. The sorbent exhibits a fairly good activity with respect to anionic dyes and satisfactory activity towards cationic dyes. This work fits into the set of 'green chemistry' rules, being convenient, non-hazardous and causing minimal damage to the environment.[27]

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.11.042.

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Table 1 Parameters of Langmuir isotherms of dye adsorption on MOF, equilibrium rate constant of pseudo first-order adsorption, and thermodynamic parameters of the adsorption.[a]

Dye	*T*/K	Parameter						
		q_m/mg g^{-1}	K_L/dm^3 mg^{-1}	R^2	*k*	ΔG^o/kJ mol^{-1}	ΔH^o/kJ mol^{-1}	ΔS^o/J mol^{-1} K^{-1}
Congo red	283	102.1	0.627	0.998	0.023	–100.25	–22.7	274.03
Congo red	292	117.4	0.724	0.999	0.027	–129.40	–34.9	323.63
Congo red	308	121.0	0.853	0.976	0.029	–142.50	–51.2	296.40
Methylene blue	283	98.4	0.527	0.985	0.019	–110.30	–54.8	196.10
Methylene blue	292	102.3	0.648	0.992	0.020	–119.84	–63.7	192.20
Methylene blue	308	117.5	0.803	0.943	0.021	–128.10	–70.2	188.00

[a] q_m is the maximum adsorption capacity of Langmuir monolayer adsorption, K_L is the Langmuir constant correlated to the adsorption energy, R^2 is the linear correlation coefficient, *k* is the equilibrium constant.

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