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Poly(methacrylic acid) based hydrogels as sorbents for removal of cationic dye basic yellow 28: Kinetics, equilibrium study and image analysis

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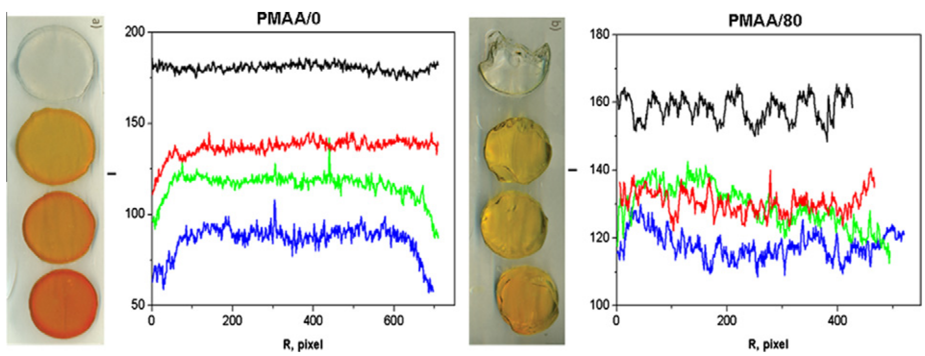
HIGHLIGHTS

- pH sensitive PMAA hydrogels are used as low-cost sorbents for cationic dye removal.
- Sorption kinetic, equilibrium, thermodynamic and image analysis experiments are done.
- Sorption data reveal spontaneous, favorable, endothermic process.
- Image analysis indicates heterogeneous coloration along hydrogel diameter.
- The saturated sorption amount of BY28 on PMAA/80 hydrogel can reach up to 157 mg/g.

GRAPHICAL ABSTRACT



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ABSTRACT

Poly(methacrylic acid) based hydrogels with neutralization degree of monomer of 0% (PMAA/0) and 80% (PMAA/80) were synthesized and their sorption potentials toward model cationic dye, basic yellow 28 (BY28), from aqueous solution, were investigated. FTIR and SEM analysis were conducted to confirm the structure and morphology of the sorbents. Investigation of the effect of the initial dye concentration, the solution pH, the sorbent mass and the temperature on sorption process, as well as the sorption kinetics and equilibrium studies were performed by batch technique. Sorption capacities of both sorbents showed to be highly sensitive to external conditions change, especially those affecting hydrogel swelling degree. Kinetic studies showed that the pseudo-first order kinetic model well fitted the experimental data and that sorption of BY28 onto PMAA hydrogels could be very well described with phase-boundary controlled models. Thermodynamical data revealed spontaneous endothermic processes. In case of PMAA/0 hydrogel physisorption was dominant, while in case of PMAA/80 hydrogel, both, the physisorption and chemisorption were presented. Langmuir, Freundlich and Dubinin–Radushkevich sorption isotherms were applied on equilibrium sorption data. The saturated sorption amount could reach up to 102 mg g^{-1} and 157 mg g^{-1} for PMAA/0 and PMAA/80 hydrogel, respectively. Image analysis proved to be useful method for analysis of uniformity of coloration along the hydrogel diameter. Both hydrogels displayed good properties in cationic dye removal, but higher sorption capacities, percentage of removed dye and significant acceleration of sorption of BY28 were accomplished by neutralizing the monomer up to 80%.

1. Introduction

Water pollution by toxic industrial waste is one of the most serious social and ecological issues of today. The use of dyes in expanding industries of textile, polymers, food and pharmaceutics

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Nomenclature

BY28	basic yellow 28
C_0	initial dye concentration (mg dm^{-3})
C_e	equilibrium sorbate (dye) concentration in solution (g dm^{-3})
C_s	amount of the sorbed dye per dm^{-3} of the solution at the equilibrium (mg dm^{-3})
C_t	dye concentration after certain sorption time t (mg dm^{-3})
E	mean free energy of sorption per molecule of the sorbate, when it is transferred from the infinity in the solution to the sorbent surface (J mol^{-1})
FTIR	Fourier transform infrared spectroscopy
I	pixel intensity of the primary color channel
I_m	mean pixel intensity of the channel of the primary color
k	kinetic model rate constant (h^{-1})
k_0	Bangham parameter (g)
K_d	distribution coefficient
K_F	Freundlich constant (mg g^{-1} dm^3 mg^{-1})$^{1/n}$
k_f	pseudo-first kinetic model rate constant (min^{-1})
k_{id}	diffusion rate constant (mg g^{-1} h$^{-0.5}$)
K_L	Langmuir sorption coefficient (dm^3 g^{-1})
k_s	pseudo-second kinetic model rate constant (min^{-1})
m_0	weight of dry hydrogel sample (xerogel) (g)
MAA	methacrylic acid
MBA	N,N′-methylenebisacrylamide
m_{eq}	weight of equilibrium swollen hydrogel sample (g)
m_s	sorbent (xerogel) weight (g)
n	Freundlich parameter
PMAA	poly(methacrylic acid)
PMAA/0	poly(methacrylic acid) based hydrogels with neutralization degree of monomer of 0%
PMAA/80	poly(methacrylic acid) based hydrogels with neutralization degree of monomer of 80%
q_e	equilibrium sorption capacity (mg g^{-1})
$q_{e,cal}$	calculated value of maximum sorption capacity (mg g^{-1})
$q_{e,exp}$	experimental value of maximum sorption capacity (mg g^{-1})
q_m	maximum sorption capacity at complete monolayer coverage (mg g^{-1})
q_t	sorption capacity at time t (mg g^{-1})
R	universal gas constant (8.314 J mol^{-1} K^{-1})
R^2	linear correlation coefficient
R_L	separation factor
SD_{eq}	equilibrium swelling degree
SEM	scanning electron microscopy
T	absolute temperature (K)
$t_{0.9}$	time at which degree of conversion reaches 0.9 (min)
t_N	normalized time
V	solution volume (dm^3)
VA-044	2,2′-Azobis-[2-(2-imidazolin-2-yl)propane] Dihydrochloride
α	Bangham parameter
α	degree of conversion
α	Elovich parameter (mg g^{-1} h^{-1})
B	Dubinin–Radushkevich parameter
β	Elovich parameter (g mg^{-1})
ΔG	change of free energy (kJ mol^{-1})
ΔH	change of enthalpy (kJ mol^{-1})
ΔS	change of entropy (kJ mol^{-1} K^{-1})
$\Delta\alpha$	range of applicability of kinetic model
ε	Polanyi potential
λ_{max}	wavelength of maximal absorption (nm)
σ	sum of squares of deviation

is accompanied by increasing volume of dyeing effluents. Thus, the synthetic dyes have become one of the major pollutants, affecting equally the human health and the aquatic ecosystem. Even in very small quantities dyes lead to changes in salinity and visible coloration of the water, reducing sunlight penetration and thus hindering the process of photosynthesis, while some of them are toxic and carcinogenic [1–3]. Very strict laws regarding elimination of dyes from wastewaters before their discharge into water streams, together with the variety and minuscule concentrations of dye molecules make their satisfactory level of removing very difficult, requiring development of various technologies for dye elimination.

The processes that are commonly used for wastewater treatment include various physical and chemical methods: flocculation [4], flotation [5], precipitation [6], coagulation [7], ion exchange [8], membrane filtration [9], electrolysis [10], photodegradation [11], extraction [12], radiation [13], oxidation [14], biological treatment [15] and sorption [16]. Despite the large number of methods, most of them are either too expensive to be applied in small plants or inefficient [17]. Low initial investment, simple design and ease of use are only some advantages that make the sorption one of the most suitable methods for dye removing, so, not surprisingly a large number of papers deal with the investigation of sorption potential of the different sorbents.

Different types of activated carbon are generally used, and therefore these are the most often investigated sorbents for removal of dyes from wastewaters [18–20]. However, their use is limited because they are expensive sorbents with high-cost regeneration, and taking into account the cost of treatment of polluted water is increasingly important.

Interest in finding adequate, cost-effective replacement with sufficient sorption capacity, sorption rate and mechanical properties has been increased extensively. Often suggested alternatives are raw materials [21,22] that are renewable or plentiful, usually used without or with minimal pretreatment; waste and by-products in various industries, agriculture and households [23] whose use reduces the cost of sorption process and contributes to the preservation of the environment; and low-cost synthetic materials (synthetic zeolites, silica-gel, hydrogels, etc.) [24,25].

Basic yellow 28 (BY28) is cationic, widely used fabric dye, which removal by sorption from aqueous solutions was investigated on only few sorbents, including granulated clay [26], bentonite [27], waste from boron industry [28], clinoptilolite [29], green alga *Caulerpa scalpelliformis* [30] and Persian kaolin [31].

Some of proposed sorbents have shown limited ability to remove the employed dye, while with the others the ability of potential development and application was noted.

In recent years, functional polymers, including poly(methacrylic acid) (PMAA) based materials, have been increasingly tested as sorbents for removal of pollutants from wastewater by way of the various possible interaction between the functional groups of polymer and pollutant. In addition, polymers have some significant advantages over other sorbent materials; for example, polymers can be readily manufactured in a wide range of physicochemical properties (form, size, size distribution, porosity, hydrophobicity, etc.) and they are tunable by inserting various ligands into the structure in order to produce specific sorbents [32–34].

Hydrogels are special type of polymeric materials with three-dimensional, weakly cross-linked structure, able to uptake and