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Magnetic hydrogel beads based on chitosan

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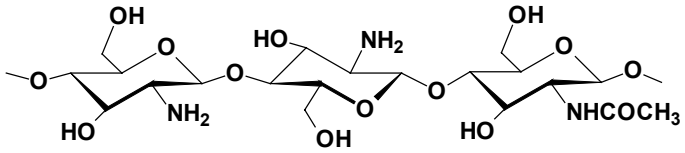
Abstract: A novel effective route for incorporating magnetic material in chitosan beads by capillary extrusion is proposed. Magnetic material (Fe_3O_4) with particle size 2 μm and 10 nm was used. The weight ratio chitosan : Fe_3O_4 was varied in the range from 4:1 to 1:1. The obtained magnetic beads were modified by physical crosslinking with $CuSO_4$, chemical crosslinking with epichlorohydrin, or were coated with a polyelectrolyte complex chitosan/poly(2-acryloylamido-2-methyl-propanesulfonic acid). The morphology and the magnetic properties of the beads were studied by optical and scanning electron microscopy, and magnetometry. The magnetisation values of the beads increased on increasing the proportion of Fe_3O_4. A magnetic field intensity of 6 kOe was completely enough to reach orientation of all dipole moments of the incorporated Fe_3O_4. The magnetic beads completely sorbed a model dye - reactive red - from its aqueous solution, thus implying that such materials might be used for wastewater treatment in textile industry.

Introduction

Ferromagnetic materials have attracted much interest due to the wide range of their potential applications. Ferromagnetic materials embedded in suitable matrices might be used in environmental applications (wastewater treatment), in biotechnology or in medicine (e.g., separation of micro-organisms, extracorporal blood detoxification, targeted drug delivery) [1-4]. Different inorganic or polymeric materials have been proposed as carriers of ferromagnetic materials. A considerable advantage of the polymeric carriers is the presence of a variety of functional groups, which enable modulating the carrier properties in function of the desired application. Due to their facile synthesis and relatively low price, different types of synthetic polymers (poly-styrene, polyacrylamide, poly(vinyl alcohol) etc.) have been used as carriers of magnetic materials [5-8]. The use of natural polymers attracts much interest not only because of their availability from abundant renewable resources, but also due to their biocompatibility and biodegradability [9,10]. The natural polyaminosaccharide chitosan has a high potential for the design of various devices for medicine, pharmacy and ecology. This is due to its unique combination of chemical, physical and biological properties - presence of reactive functional groups, water-solubility and non-toxicity [11].

From a technological viewpoint, the solubility of chitosan determines the ease of preparation of chitosan beads/capsules, films, gels, powders, fibres, granules, tablets, and sponges [12-17]. All these facts, in conjunction with the ability for

reversible interactions between chitosan and substances with suitable functional groups, make chitosan a promising carrier of magneto-sensitive materials. Microbeads of chitosan and Fe_3O_4 have been prepared by suspension crosslinking using glutaraldehyde as a crosslinking agent [18]. The best magnetic properties of these beads are at 10 kOe magnetic field intensity. Similar chitosan magnetic particles successively crosslinked with glutaraldehyde and epichlorohydrin (ECC) have been studied aiming at enzyme (trypsin) purification [19].



Scheme 1. Segment of a chitosan chain

In the present study a simple and efficacious method for embedding magnetic material (Fe_3O_4) in different modified chitosan beads has been applied. The effect of the type of crosslinking (physical or chemical) and of the coating with the polyelectrolyte complex (PEC) chitosan/poly(2-acryloylamido-2-methylpropanesulfonic acid) (PAMPS) on the magnetic properties and the equilibrium degree of swelling of the prepared hydrogel beads has been studied. The prepared magnetic beads have been used for sorption of a model reactive dye.

Results and discussion

Beads characterisation

Magnetic chitosan hydrogel beads were prepared by simple coacervation involving capillary extrusion of chitosan solution containing different amounts of magnetite. The formation of the beads is due to the conversion of the water-soluble protonated $-NH_3^+$ form of chitosan to the water-insoluble neutral $-NH_2$ form. The beads, as prepared, will be denoted as 'coacervate' in order to be distinguished from 'swollen' ones, which, once dried, have been swollen to reach equilibrium swelling. The coacervate and the swollen beads were transparent and flexible. The main types of the obtained magnetic chitosan beads after freeze-drying are shown in Fig. 1.

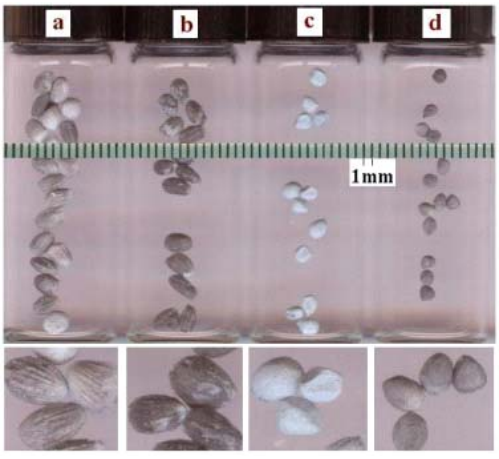


Fig. 1. Freeze-dried magnetic chitosan beads: (a) non-crosslinked; (b) crosslinked with ECC; (c) crosslinked with $CuSO_4$; (d) coated with PEC chitosan/PAMPS

The average diameter of the magnetic chitosan beads depended both on the ratio [chitosan] : [Fe_3O_4] and on the used modifying agent. As seen from the results presented in Tab. 1, the beads had the smallest diameters when prepared by coating with PEC chitosan/PAMPS.

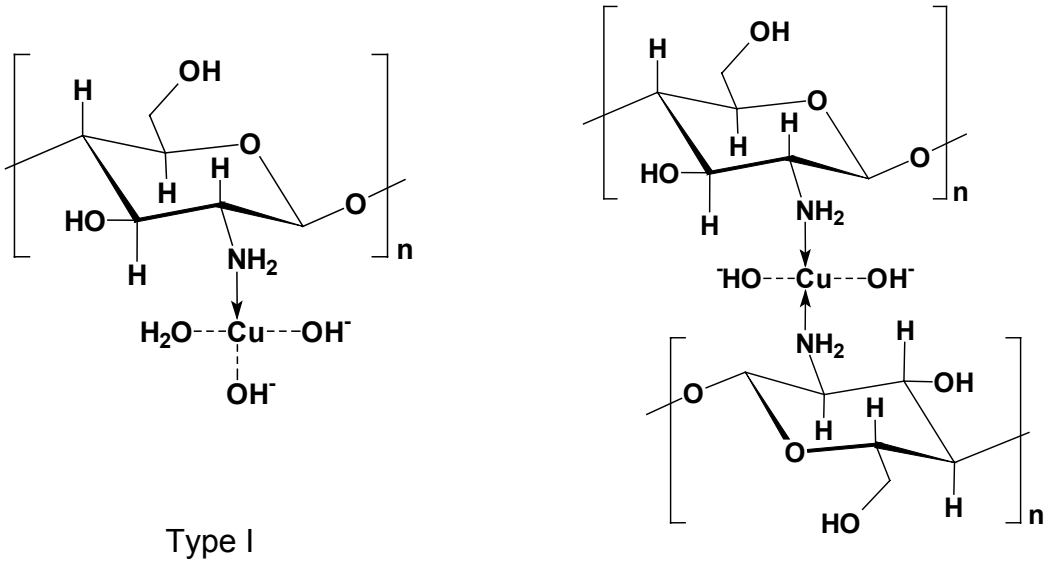
Tab. 1. Characteristics of the magnetic chitosan beads

Bead type	Average weight, mg		Average diameter, mm	
	coacervate	dry	coacervate	dry
	[chitosan] : [Fe_3O_4] = 1:1			
chitosan	12	0.61	2.50	0.96
chitosan/PAMPS	3	0.65	1.43	0.85
chitosan/$CuSO_4$ [a]	9	0.79	2.25	0.92
chitosan/ECC [b]	13	0.66	2.26	0.87
	[chitosan] : [Fe_3O_4] = 2:1			
chitosan	5	0.24	2.10	1.14
chitosan/PAMPS	2	0.23	1.51	0.68
	[chitosan] : [Fe_3O_4] = 4:1			
chitosan	4	0.21	2.21	1.22
chitosan/PAMPS	2	0.21	1.37	0.64

[a] [$CuSO_4$] : [aminoglucoside unit] = 1.5:1. [b] [ECC] : [aminoglucoside unit] = 5:1.

The non-crosslinked magnetic chitosan beads were flexible, insoluble in neutral and alkaline medium, and soluble in acidic medium. A higher mechanical stability of the beads was achieved by crosslinking with ECC or $CuSO_4$. After crosslinking with ECC the coacervate beads remained flexible and their size changed insignificantly. The beads crosslinked with ECC did not dissolve in acidic medium. Crosslinking with $CuSO_4$ caused an insignificant decrease of the beads size relative to that of the non-crosslinked beads (Tab. 1), and they got a shade of blue colour (Fig. 1c). Probably, the reason for this colour change is the complex formation between Cu^{2+} ions and chitosan macromolecules. It is known that chitosan forms complexes with different metal ions. The optimum pH values for complex formation between chitosan and Cu^{2+} ions are in the range from 5 to 7 [21]. The structure of the complex chitosan/ Cu^{2+} is presented in Scheme 2.

In the pH range 5 - 5.8, complex I is more stable and for pH values higher than 5.8 complex II is predominant. After immersion of the magnetic chitosan beads in PAMPS aqueous solution an abrupt decrease of the beads size was observed. Such decrease was formerly observed in the case of chitosan beads [22] and was attributed to the PEC formation between chitosan and PAMPS on the surface layer of the beads. The average diameter of the non-crosslinked coacervate beads and dry beads decreased up to the 1.7-fold after coating with PEC (Tab. 1).



Scheme 2. Structure of the formed complex between chitosan and Cu^{2+} ions according to ref. [21]

Surface morphology of the magnetic chitosan beads

Scanning electron micrographs of different types of magnetic chitosan beads are shown in Fig. 2. The surface of the unmodified magnetic chitosan beads is filamentous and highly porous (Fig. 2A). Such structure provides very good sorption properties of the beads. The porous structure is well seen on the cleavage surface of the bead (Fig. 2B). The surfaces of the beads, coated with PEC chitosan/PAMPS (Fig. 2C), and also of those crosslinked with Cu^{2+} ions (Fig. 2D), differ considerably from those of the non-crosslinked chitosan beads. As seen, they are less porous, which in the first case is due to the complex formation between chitosan and PAMPS, and in the second to the formation of a physical network resulting from the crosslinking with Cu^{2+} ions.

Swelling degree of the magnetic chitosan beads

It was found that α_{eq} values of the magnetic chitosan beads depended on the amount of chitosan, on the way of beads modification and on the pH value of the medium. The α_{eq} values of the prepared magnetic chitosan beads at different pH (4, 7 and 9) and at constant ionic strength (I = 0.1) are given in Tab. 2. As seen, the α_{eq} value was the highest in the case of non-crosslinked chitosan beads. Chemical crosslinking with ECC led to a loss of their solubility in acidic medium and to decrease of α_{eq} in neutral and alkaline medium. For example, at pH 7, α_{eq} decreased in the order: non-crosslinked beads > coated with PEC chitosan/PAMPS > crosslinked with ECC ≈ crosslinked with Cu^{2+} ions. In the case of magnetic chitosan beads crosslinked with ECC, α_{eq} decreased in the order: pH 4 > pH 7 > pH 9. At pH 4, fragmentation and dissolving of the beads, physically crosslinked with Cu^{2+} ions, was observed. This is a result of the destruction of the complex between Cu^{2+} ions and chitosan macromolecules at pH < 5.3.

The effect of the pH value on the swelling degree of the beads was explained with the degree of ionisation of chitosan. It is known that chitosan is a weak polybase with pK_a = 6.5 [23]. At pH 4, practically all (99.9%) of the amino groups of chitosan are

protonated, while at pH 7 it is 24%, and at pH 9 about 0.3%. The beads swelled at the greatest extent in acidic medium, which is related to the repulsion of the positive charges in chitosan macromolecules.

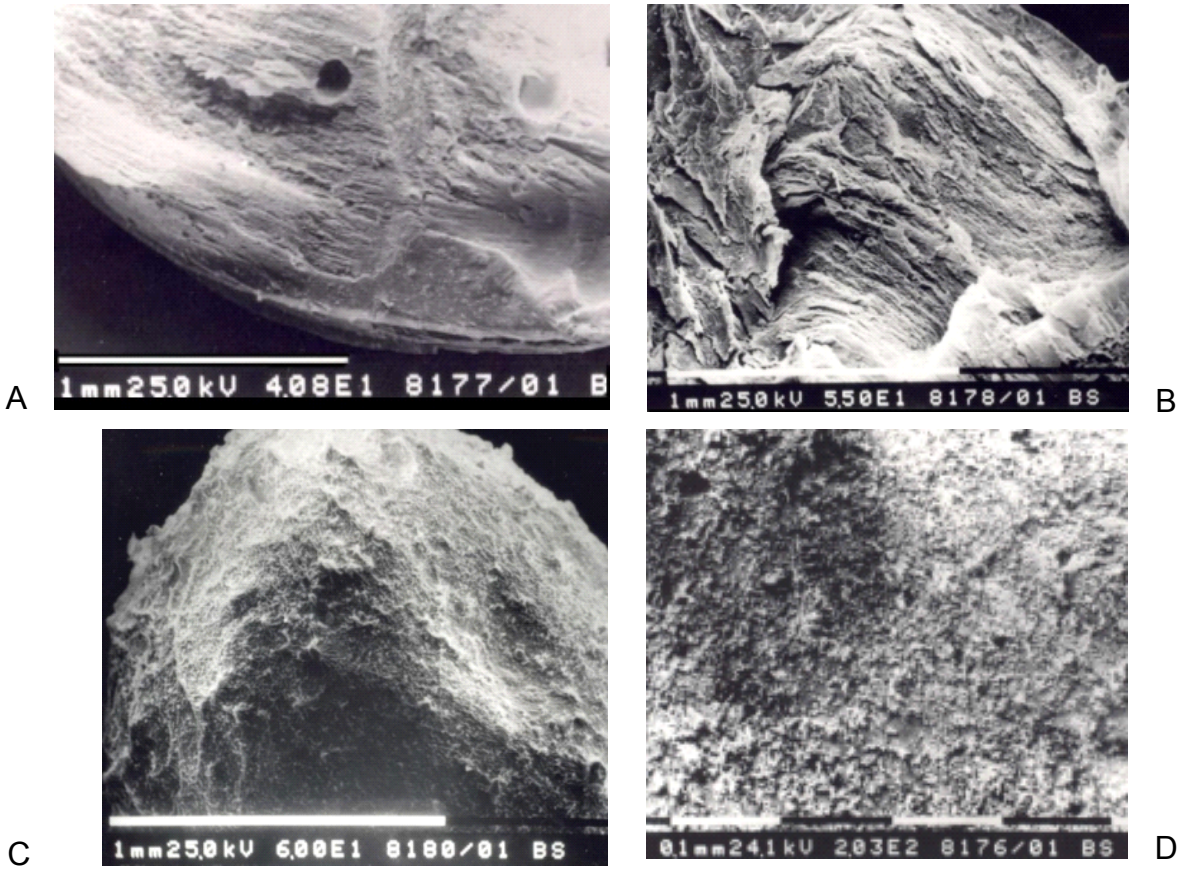


Fig. 2. SEM micrographs of freeze-dried magnetic chitosan beads: non-crosslinked, magnification ×40 (A), and breakage ×55 (B); coated with PEC chitosan/ PAMPS, magn. ×60 (C); crosslinked with Cu^{2+} ions, magn. ×200 (D); [chitosan] : [Fe_3O_4] = 1:1

Tab. 2. Dependence of the equilibrium degree of swelling (α_{eq}) of magnetic chitosan beads on pH; 25°C; *I* = 0.1; [chitosan] : [Fe_3O_4] = 1:1

Bead type	α_{eq}, %		
	pH 4	pH 7	pH 9
chitosan	[a]	400	180
chitosan/PAMPS	[a]	120	[b]
chitosan/ECC	63	30	20
chitosan/$CuSO_4$	[a]	30	20

[a] The beads dissolved. [b] PEC chitosan/PAMPS is not stable at pH > 8.

Magnetic properties

The magnetic properties of dry beads were evaluated by measurement of magnetisation of the beads as a function of magnetic field intensity with a vibrating-sample

magnetometer. In all measurements beads containing a constant amount of magnetite were used. The ratio [chitosan] : [Fe_3O_4] was varied in the range 4:1 to 1:1 in order to investigate the effect of the ratio diamagnetic/ferromagnetic material onto the magnetisation of the beads. The highest magnetisation was determined for magnetic chitosan beads at weight ratio [chitosan] : [Fe_3O_4] = 1:1 (Fig. 3). As expected, on decreasing the amount of the ferromagnetic material incorporated in the beads the magnetisation decreased. The experimentally found values of magnetisation were lower than the calculated ones. This lowering probably was due to the losses of ferromagnetic material because of sedimentation of the dispersed ferromagnetic material. Such sedimentation occurred regardless of the relatively high chitosan solution viscosity. The obtained data permitted corrections to be made for the actual Fe_3O_4 content in the dry beads. For feed ratios [chitosan] : [Fe_3O_4] = 1:1, 2:1 and 4:1, the experimentally found weight ratios were 20, 21 and 12% lower, respectively.

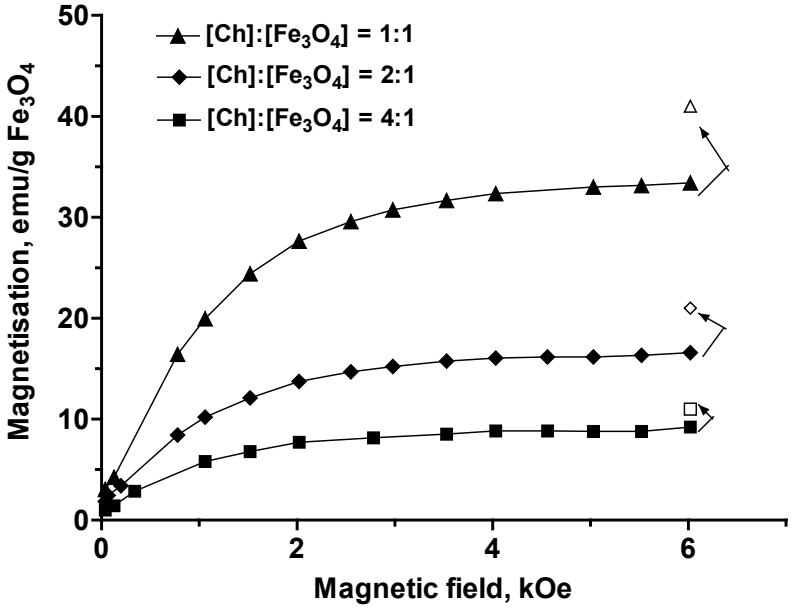


Fig. 3. Magnetisation (emu/g) vs. applied magnetic field (kOe) for non-crosslinked magnetic chitosan beads at different weight ratios [chitosan] : [Fe_3O_4]. Magnetisation values calculated from the feed ratios (empty symbols) are presented for comparison. Fe_3O_4 particle size: 2 μm

The effect of the particle size of the magnetite involved in the beads is shown in Fig. 4. The magnetic properties of the beads, containing magnetite with two different particle sizes, 2 μm and 10 nm, at different weight ratios [chitosan] : [Fe_3O_4] = 1: 1 and 4: 1, respectively, were studied. As seen, the beads with embedded nanosized Fe_3O_4 reached saturation at lower applied magnetic field values (from ≈1.5 to 3.5 kOe) than those containing the micro-sized magnetite in the same amount.

For the beads containing Fe_3O_4 with particle sizes 2 μm, a magnetic field of intensity ≈6 kOe was required for the saturation level to be reached. For all of the prepared beads, a magnetic field with intensity 6 kOe was completely enough for the orientation of all dipole moments of 0.06 - 0.08 g magnetic chitosan beads, containing 0.03 g magnetite. The action of a magnet on the magnetic chitosan beads is illustrated in Fig. 5. The coacervate beads, which are 20-fold heavier than the dry ones, were easily moved with the same magnet, which moved the dry beads.

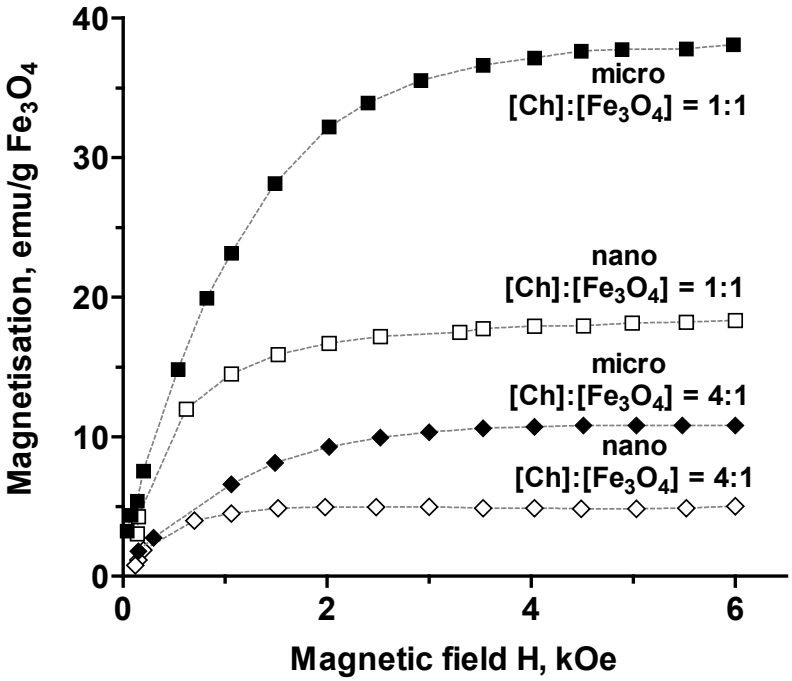


Fig. 4. Magnetisation (in emu/g) vs. applied magnetic field (in kOe) for non-cross-linked chitosan microspheres, containing micro- (2 μm) and nanosized (10 nm) Fe_3O_4 at different weight ratios [chitosan] : [Fe_3O_4]

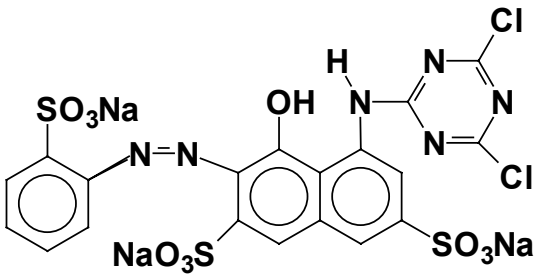
A B

Fig. 5. Action of a magnet on coacervate (A) and dry magnetic chitosan beads (B) at the weight ratio [chitosan] : [Fe_3O_4] = 1:1. The average weight of a coacervate magnetic chitosan bead is 12 mg, and of a dry one it is 0.61 mg

Sorption of the model dye reactive red (RR) by different types of magnetic chitosan beads

The pollution of wastewater with dyes toxic for humans and warm-blooded animals from the textile industry is an important ecological problem that necessitates development of suitable methods for their removal. The sorption process is one of the effective methods for water purification. It is known that chitosan possesses high affinity for different dyes – reactive, acid, vat, sulfur, disperse and naphtol [11,24,25].

Reactive red dye (RR) was used as a model dye. It contains three sulfo groups in its molecule able to interact ionically with chitosan amino groups. The interaction of the chitosan beads with RR led to red-coloured beads. The RR sorption in the beads was qualitatively followed by the decrease of the adsorption intensity in the visible spectrum of the dye.



Scheme 3. Reactive red dye (RR)

It was found that all of the beads, with exception of those coated with PEC chitosan/ PAMPS, sorbed the model dye completely in 5 h (Fig. 6). The magnetic chitosan beads, coated with PEC chitosan/PAMPS, sorbed the dye at significantly lower rate. In this case, a complete dye sorption was achieved after 72 h. The low sorption rate in this case might be explained by the formation of the PEC on the beads' surface. The PEC hampers the dye sorption from the surface to the bead bulk. An interesting feature was observed studying the dye sorption from magnetic chitosan beads, crosslinked with $CuSO_4$. A change in the dye spectrum has been observed – the double characteristic maxima at λ = 513 and 535 nm transformed to a new one at 526 nm wavelength. This is due to the Cu^{2+} salts of the dye, which are formed by the interaction between Cu^{2+} ions and RR sulfo groups. Kinetics of the sorption was studied at a high excess of chitosan – at mole ratio $[NH_3^+]$: $[SO_3^-]$ = 32:1. The dependence of the sorbed RR amount (Q_t) on the time of sorption is shown in Fig. 6. The sorption rates (V) were calculated from the initial slopes.

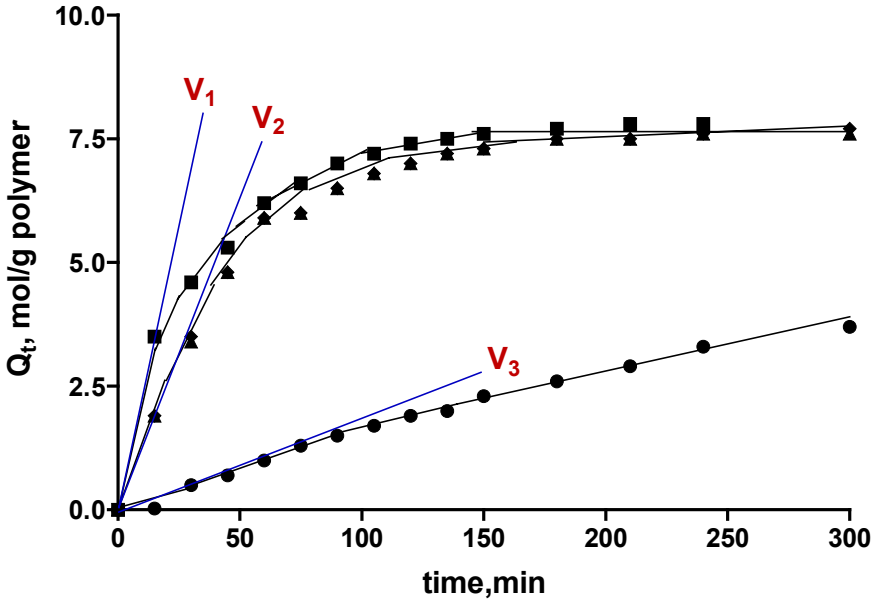


Fig. 6. Amount of sorbed RR dye by magnetic chitosan beads as a function of time: non-crosslinked (■); crosslinked with ECC (♦); crosslinked with $CuSO_4$ (▲); coated with PEC chitosan/PAMPS (●); [chitosan] : $[Fe_3O_4]$ = 1:1; 25°C

The following values were determined for the different types of magnetic chitosan beads: $V_1 = 3.88\times10^{-2}$ mol·g^{-1}·s^{-1} (non-crosslinked), $V_2 = 2.07\times10^{-2}$ mol·g^{-1}·s^{-1} (both crosslinked with ECC and $CuSO_4$), and $V_3 = 2.17\times10^{-3}$ mol·g^{-1}·s^{-1} (coated with PEC

chitosan/PAMPS). The lower sorption rate in the case of magnetic chitosan beads coated with PEC might be explained with the decreased amount of free amino groups on the beads surface due to the PEC formation. This assumption was supported by the fact that the whole bulk of the magnetic beads coated with PEC chitosan/PAMPS was dyed in contrast to the non-crosslinked ones, which were dyed only on their surface. It was found that the equilibrium sorption of RR from magnetic chitosan beads crosslinked with ECC was reached at the mole ratio [chitosan] : [RR] = 1.3:1.

The obtained results show that chitosan is a suitable carrier of magnetite and the chitosan-based magnetic beads might be used successfully for wastewater treatment for the removal of toxic substances, which can interact ionically with the natural polymer. The prepared magnetic carriers might find applications also in medicine and biotechnology because of the biocompatibility, biodegradability and non-toxicity of chitosan.

Experimental part

Materials

High-molecular weight chitosan (MW 6×10^5; degree of deacetylation 80%), and the crosslinking agents epichlorohydrin (ECC) and $CuSO_4 \cdot 5\ H_2O$ were purchased from Fluka. Magnetite (Fe_3O_4) with particle size ≈2 μm and ≈10 nm was used. Poly(2-acryloylamido-2-methylpropanesulfonic acid) (PAMPS) with viscosity-average molecular weight $9.8\cdot10^5$ was prepared by radical polymerisation as previously described [20]. All used reagents were of analytical grade of purity. The following buffer solutions were used: pH 4.0 (CH_3COOH/NaOH), pH 7.0 (KH_2PO_4/Na_2HPO_4) and pH 9.0 ($NaHCO_3$/Na_2CO_3). Reactive red (RR) was kindly supplied by Prof. T. Konstantinova, UCTM, Sofia.

Preparation of magnetic chitosan beads

Different amounts of Fe_3O_4 were added into 1.5% chitosan solution in 0.5% acetic acid. The weight ratio [chitosan] : [Fe_3O_4] was 1:1, 2:1 and 4:1. The obtained homogeneous viscous mixture was dropped through a capillary (diameter 0.5 mm) into 5% aqueous NaOH. Spherical chitosan particles were formed. The obtained magnetic beads were kept in the precipitation alkaline bath for 24 h. After that they were washed repeatedly with distilled water until neutral reaction of the aqueous phase.

Coating of the coacervate beads with polyelectrolyte complex (PEC) chitosan/PAMPS was carried out by immersion of the beads in 3% aqueous solution of PAMPS at room temperature for 2 h. After that the coated beads were washed repeatedly with distilled water for complete removal of unreacted PAMPS.

Magnetic chitosan beads (weight ratio [chitosan] : [Fe_3O_4] = 1:1) were physically crosslinked in aqueous solution of $CuSO_4$ at room temperature for 24 h (mole ratio [$CuSO_4$] : [aminogucoside units] = 1.5:1). Chemically crosslinked chitosan beads were prepared in alkaline solution of ECC (0.04 M). The reaction was carried out at 40°C for 3.5 h (mole ratio [ECC] : [aminoglucoside units] = 5:1). The physically or chemically crosslinked beads were washed repeatedly for removing the unreacted crosslinking agent.

Magnetic beads characterisation

The average bead diameter from 10 measurements was determined using a Reichert-Zetopan microscope. Beads surface morphology was observed by means of a Philips SEM 515 scanning electron microscope. Specimens were placed on the sample holders with a double-sided adhesive tape, vacuum-coated with carbon and gold film and then observed.

Equilibrium degree of swelling of the magnetic beads

The equilibrium degree of swelling (α_{eq}) was determined by immersion of dry and previously weighed beads into buffer solutions (pH 4, 7 or 9, ionic strength I = 0.1) at 25°C. At certain intervals of time, after gentle removal of the excess of buffer solution, the beads were weighed. This procedure was repeated until reaching a constant weight of the swollen beads. α_{eq} was estimated by the equation:

$$\alpha_{eq} \text{ (in \%)} = 100 \times (W_{eq} - W_d) / W_d$$

where W_{eq} and W_d were the weights of the sample in equilibrium swollen and in dry state, respectively. The results are averages from three measurements.

Magnetic properties

The magnetisation of the obtained magnetic chitosan beads was measured with a vibrating-sample magnetometer (Laboratory of Electricity and Magnetism, Department of Physics, University of Sofia). Dry magnetic chitosan beads (100 beads, $m_{Fe_3O_4} = 30.7$ mg) were fixed in quartz holders, which were placed in the magnetometer. Magnetisation of the beads was then determined by applying an increasing magnetic field and the results were used to calculate the magnetic quality of the beads.

Sorption kinetics of a model dye – reactive red

The electronic spectrum of RR was registered with a spectrophotometer UV-VIS SPECORD 71, and the concentrations of the RR aqueous solutions were determined by calibration curves at the following absorption maxima: $\lambda_{max,1}$ = 513 nm, and $\lambda_{max,2}$ = 535 nm. The sorption kinetics of RR from different types of chitosan beads was evaluated spectrophotometrically. The chitosan beads were immersed in 10 ml RR aqueous solutions with initial concentration $9.83 \cdot 10^{-5}$ M. The amount of the sorbed dye was calculated by the equation:

$$Q_t = V (C_0 - C_t) / m_{Ch}$$

where C_0 is the initial concentration of RR solution (in mol/l); C_t the concentration of RR solution at the moment t during sorption (in mol/l); V the volume of RR solution (in l); m_{Ch} the weight of the beads included in chitosan (in g).

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