Heavy metal removal from wastewater by ferrogels

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The presence of heavy metals in water / wastewater is a very serious issue for the environmental protection and managing. Main sources of uncontrolled emission of these metals include mine and metallurgical industry. Heavy metals even at low concentrations have very high toxicity for living organisms. This work demonstrates a newly developed method for the effective removal of some heavy metals (copper and silver) by accumulating them in the gel structure loaded with the sorption material. The selection, and then synthesis, of a gel matrix for sorbent particles was the essential step in the experimental work. Gel materials represent a rather unusual way in which a large amount of liquid can be kept “solid”, and therefore gels possess properties characteristic for both: liquids and solids. The hydrogel poly(N-isopropylacrylamide) (pNIPA gel) acted as the matrix for sorbent particles. The pNIPA gel undergoes discontinuous volume phase transition induced by the change in temperature. At temperature $34^\circ C$ it passes from the swollen state to the shrunken state by releasing a large amount of the solution from the polymeric network. The gel matrix allowed iron (II,III) oxide (sorbent (Gialdo et al., 2013)) to be homogenously spread throughout the system. Magnetite particles loaded into the gel matrix formed a ferrogel material, which could be controlled by the external magnetic field.

The synthesis of the pNIPA ferrogel involved the following steps:
1. Free-radical polymerization of NIPA using well documented procedures (Filipcsei et al., 2007)
2. Purification and drying the resulting polymeric material (pNIPA)
3. Grinding the pNIPA material to a fine powder
4. Mixing the pNIPA powder with known amount of ferromagnetic particles (e.g. nanosized magnetite) – the preparation of the ferro-pNIPA system
5. Swelling the ferro-pNIPA system in the aqueous solution containing known concentration of cationic forms of heavy metals – the formation of the pNIPA ferrogel swollen by the aqueous solution (Figure 1)

![Figure 1. The sample of ferrogel swollen in Ag⁺ aqueous solution.](image)

The temperature-induced volume phase transition of the prepared pNIPA ferrogel samples was the key feature that allowed one to study quantitatively the sorption properties of the gel materials. Above the temperature at which pNIPA ferrogels undergo volume phase transition (slightly above $34^\circ C$) the aqueous solution was released from the gel structure. The solution was then analyzed using ICP-MS technique and the sorption efficiencies of ferrogel with respect to copper and silver were quantitatively determined. The released solution was separated from the sorption system in the external magnetic field. 4% pNIPA ferrogel containing 12% (w/w) Fe₃O₄ removed 52% of Cu and 100% of Ag (Figure 2) from aqueous solutions. It turned out also that the presence of gel matrix increased slightly the sorption efficiency of magnetite.
It is worth emphasizing that the method developed takes advantage of both: the temperature-induced volume phase transition of the gel system and its magnetic properties that make the whole sorption system responsive to the external magnetic field. In addition to this the experimental studies revealed larger sorption efficiencies of the pNIPA-magnetite gel system compared to magnetite alone. The ferrogel sorption system is stable over a wide range of temperature and pH and can be easily restored via the swelling – shrinking cycling.

References