Removal of cobalt ions from aqueous solutions by polymer assisted ultrafiltration using experimental design approach. part 1: Optimization of complexation conditions

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ABSTRACT

The polymer assisted ultrafiltration process combines the selectivity of the chelating agent with the filtration ability of the membrane acting in synergy. Such hybrid process (complexation–ultrafiltration) is influenced by several factors and therefore the application of experimental design for process optimization using a reduced number of experiments is of great importance.

The present work deals with the investigation and optimization of cobalt ions removal from aqueous solutions by polymer enhanced ultrafiltration using experimental design and response surface methodological approach. Polyethyleneimine has been used as chelating agent for cobalt complexation and the ultrafiltration experiments were carried out in dead-end operating mode using a flat-sheet membrane made from regenerated cellulose. The aim of this part of experiments was to find optimal conditions for cobalt complexation, i.e. the influence of initial concentration of cobalt in feed solution, polymer/metal ratio and pH of feed solution, on the rejection efficiency and binding capacity of the polymer. In this respect, the central compositional design has been used for planning the experiments and for construction of second-order response surface models applicable for predictions. The analysis of variance has been employed for statistical validation of regression models. The optimum conditions for maximum rejection efficiency of 96.65% has been figured out experimentally by gradient method and was found to be as follows: $[Co^{2+}]_0 = 65$ mg/L, polymer/metal ratio = 5.88 and pH 6.84.

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1. Introduction

In the last quarter of a century, the presence of heavy metal ions in the environment has received extensive attention due to increased discharge, their non-biodegradable properties, toxicity in the environment, and other adverse effects which heavy metal ions have on receiving waters [1]. Cobalt is a ferromagnetic metal that has a large application in different industrial fields such as production of corrosion-resistant alloys and super-alloys for parts in gas turbine aircraft engines, magnets and magnetic recording media, catalysts for the petroleum and chemical industries as well as pigments [2]. It is also applied in the electroplating industry because

of its appearance, hardness, and resistance to oxidation. Cobalt radioisotope Co^{60} is a radioactive substance that is used in medicine for radiotherapy, as well as in a number of industrial applications. All these applications of cobalt in industry and medicine represent the potential sources for generation of wastewater streams laden with cobalt. Although cobalt is an essential element for life in tiny amounts (central component of vitamin B_{12}), at higher levels of exposure it shows carcinogenic effects similar to nickel [2].

Thus, it is indispensable to treat metal-contaminated wastewaters prior to their discharge to the environment. Various treatment techniques for wastewater laden with heavy metals ions have been developed in the last decade both to reduce the amount of wastewater produced and to improve the quality of the treated effluent [1]. Although different treatment methods such as chemical precipitation [3,4], coagulation–flocculation [4–6], electrochemical processes [7,8], ion exchange [8,9] and sorption [10–13] can be employed to remove heavy metals from wastewaters, they have their intrinsic advantages and drawbacks in application. For instance, chemical precipitation and coagulation–flocculation as well as electrochemical treatment become ineffective particularly when metal ion concentration in the solution is low (1–100 mg/L). These processes produce large quantity of sludge to be treated. Ion

Nomenclature

a	the weight of polymer (g)
b_0, b_i, b_{ii}, b_{ij}	regression coefficients in polynomial equation
$\bar{b}$	$(L \times 1)$ vector of regression coefficients of response surface model
C	concentration of Co^{2+} in feed solution, $[Co^{2+}]_0$ (mg/L)
C_p	concentration of Co^{2+} in permeate flux (mg/L)
DF	degree of freedom
e	residual error
F-value	ratio of variances, computed value
h	number of independent variables
i and j	subscripts (integer variables)
J	permeate flux
k	superscript, indicating the iteration of searching in gradient method
L	number of regression coefficients within RS-model
$\bar{m}$	vector indicating the direction of steepest ascent of the objective function
m_i	component of the direction vector
MS	mean square
M_W	molecular weight
N	number of experimental runs in CCD
P-value	statistical estimator
R^2	coefficient of multiple determination
R^2_{adj}	adjusted statistic coefficient
r	ratio of polymer (PEI) to cobalt (Co^{2+}) (w/w)
SS	sum of squares
s	integer number for adjusting the step-length in gradient method
t	time
u	number of design variables
$\bar{\bar{X}}$	$(N \times L)$ design matrix of the independent variables levels
$\bar{x}_S$	vector of stationary point coordinates in coded terms
$\bar{x}^{(k)}$	vector of design variables in coded terms
x_1, x_2, x_3	coded levels of the factors (design variables)
$\bar{Y}$	$(N \times 1)$ vector of the experimental observations (rejection efficiency)
Y	rejection efficiency (experimental value);
$\hat{Y}$	rejection efficiency (predicted value by RS-model);
z_1, z_2	actual variables
*	superscript indicating optimal values of variables;

Greek letters

α	axial point or "star" point in CCD;
λ	step-length of searching in gradient method
$\omega_1, \omega_2, \omega_3$	canonical axes with origin in stationary point
Ω	valid region (initial region of experimentation)

exchange and activated carbon sorption processes are extremely expensive, especially when treating a large amount of wastewater containing low heavy metal concentration. As regards the low-cost sorbents, it should be pointed out that despite their properties of being inexpensive and easily available they have relatively low binding capacity [13]. Therefore nowadays there is a growing interest in developing and optimization of the alternative and promising methods for the removal of heavy metals from wastewaters. In this respect, the membrane enhanced ultrafiltration assisted by complexation using different water-soluble polymers has received a considerable attention for the treatment of inorganic effluent, since

it is capable of efficient treatment of different wastewaters streams laden with heavy metals ions and radionuclides [14–28].

Polymer assisted ultrafiltration (PAUF) is a hybrid process that combines two phenomena, i.e. binding of metal ions to a water-soluble polymer (complexation) and ultrafiltration. Since the pore sizes of ultrafiltration membranes are not appropriate to separate heavy metal ions, the chelating agents are used for binding the metals and to form macromolecular complexes [26–28]. These complex molecules, having a higher molecular weight than the molecular-weight-cut-off (MWCO) of the membrane, will be retained, while the non-complexed ions pass through the membrane. By means of PAUF method and using different water-soluble polymers it is possible to achieve selective separation and recovery of heavy metals with low energy requirements [26]. Highly purified permeates have been achieved using PAUF method [14–29]. Generally, the results regarding polymer assisted ultrafiltration were reported for different wastewater streams containing various species of heavy metals (Cu, Zn, Cd, Co, Ni, Pb, Fe, Cr, Mn, Hg) and different water-soluble metal-binding polymers such as polyacrylic acid (PAA), polyethyleneimine (PEI), polyvinylalcohol (PVA), polyacrylic acid sodium salt (PAASS), poly(dimethylamine-co-epichlorohydrin-co-ethylene-diamine) (PDEHED) and so forth [14–28]. The progress in macromolecular chemistry such as the invention of dendritic polymers is providing novel opportunities to develop the efficient nanoscale chelating agents for environmental and industrial applications [29]. The results presented in the reference [29] indicate that the dendrimer-enhanced ultrafiltration (DEUF) is a promising process for removal and recovery of metal ions from aqueous solutions. Another option of enhanced ultrafiltration to remove efficiently heavy metals from wastewaters deals with micellar-enhanced ultrafiltration (MEUF). This separation technique involves the addition of surfactants to contaminated aqueous solution [30–35].

Recently, the design of experiments (DoE) and response surface methodology (RSM) has been proved to be effective tools for investigation, modeling and optimization of the enhanced ultrafiltration processes. In our previous work [25] we have applied the experimental design and RSM for the optimization of hybrid complexation–ultrafiltration process for copper removal from aqueous solutions taking into account the feed concentration of polyacrylic acid (i.e. chelating agent), the pH value and the polymer to metal ratio. A good conformity was observed between the predicted and the experimental optimal conditions of polymer assisted ultrafiltration. Xiarchos et al. [35], has applied response surface methodology for the modeling of copper removal from aqueous solutions using micellar-enhanced ultrafiltration. Also, Aydiner et al. [36] applied the Taguchi experimental design to investigate the influence of factors upon on nickel rejection, surfactant rejection and steady-state flux in a surfactant-added powdered activated carbon/microfiltration hybrid process.

The present work deals with application of DoE and RSM tools for modeling and optimization of cobalt removal from aqueous solution using polymer assisted ultrafiltration process and PEI as chelating agent. The task of dead-end ultrafiltration experiments was to optimize the complexation conditions in order to ensure the maximum rejection efficiency. The optimum conditions will be applied in real ultrafiltration systems operated in cross-flow mode.

2. Materials and methods

2.1. Chemicals

All the chemicals used in experiments were of analytical reagent grade. As a source of cobalt ions, cobalt (II) chloride hexahydrate $CoCl_2 \cdot 6H_2O$ (puriss) ($M_W = 237.93$ g/mol) provided