THE RECOVERY OF STREPTOMYCIN FROM INDUSTRIAL EFFLUENTS

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Abstract: *The application of Purolite A-510 anionic resin for an industrial effluent treatment generated by the technological process of streptomycin production is studied taking into account the recycling requirements of treated wastewater and recovery demands of all useful materials (e.g., solvents, antibiotics etc.). All the experiments were performed on a laboratory set-up scale by working into static and dynamic regime in order to establish the optimal operational conditions (e.g., pH, operational time, flow rate, drug concentration) for high removal efficiencies of streptomycin. The streptomycin removals using the Purolite A-510 resin correspond to values of 62.93 - 96% for different operational conditions.*

Keywords: *ionic exchange, Purolite A-510, effluent, streptomycin.*

1. Introduction

The ion exchange process is a suitable chemical method of reducing unwanted salt loads in wastewaters and removing toxic constituents [3], [4], [14]. This process can also be employed for the detoxification of dilute ionic solutions and in the recovery of raw materials or costly materials (e.g., removing specific toxic ions or nutrients such as NH_4^+ if the environmental hazards are great; decolourization of solutions; oxidation and reduction reactions at groups derived from quinones, malachite green or thionine dyestuffs; separation of isomeric compounds at optically active groups; binding of cationic, anionic or non-ionic organic substances such as dyes, humic acids and detergents etc. [3], [5], [14]). Mechanism and fundamental theory associated with ion exchange are basically similar to an adsorption process in which a solid, usually porous, particle with reactive sites on its surface comes to equilibrium with ions in solution [5]. The sites have an exchangeable ion such as H^+, HO^-, Na^+, or Cl^- attached. When placed in an aqueous media having ions with a stronger affinity for the reactive (adsorption) site than the attached group, an exchange process takes place that results in equilibrium with the stronger affinity groups predominating on the adsorption sites.

The synthetic ion exchangers (e.g. specific ion, selective ion, amphoteric ion exchangers, redox exchangers, optically active exchangers, adsorbent resins [4]) employed consist of a stable matrix onto which acidically or basically reacting groups are attached, which are capable of exchanging cations or anions respectively (hence cation and anion exchangers). The choice of the particular ion exchanger depends on the solution *pH*. Anion exchangers can take up ions in the strongly acidic (e.g., operating within the *pH* range 1-13) to the weakly basic range (e.g.,

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operating up to about *pH* 8). The ion exchangers are stable up to about 70 °C (strongly basic ones) or 120 °C (acid exchangers). The reaction velocity and reaction equilibrium are decisive in ion exchange.

The ion exchange can be employed in removing of organic bases or drugs from industrial effluents or recovery of metals or other raw materials from different kind of aqueous media.

Due to the polar nature of their functional groups, most commonly used drugs are relatively easy to remove by sorption on various materials: activated carbon, non ionic or ionic synthetic polymers, biomass-based exchangers, anionic clay mineral and also adsorbents [8]. The drug binding potential of these materials is affected by physic-chemical characteristics of both sorbent and drug, their compatibility, as well as the operational conditions (particle size of granulated sorbent, *pH*, ionic strength, temperature, wastewater flow rate etc.) [1], [2]. The economic use of various sorbents in removing drugs from industrial effluents, but also a better understanding of these processes in natural systems require information on the drug uptake.

This work continues our studies concerning employment of some anionic exchangers for removing of some organic compounds [1], [7], [9-13]. In this context, an anionic exchanger strongly basic (the ionic form being Cl^-) Purolite A-510 was tested in recovery of drugs (i.e. *streptomycin*) from industrial wastewaters (i.e. effluents from industrial production of drugs). Ion exchange is employed in conjunction with other methods for industrial wastewater treatment. Usually, this process proceeds wastewater sedimentation and filtration or different liquid/liquid extractions.

The ion exchange experiments were performed as function of *pH*, initial drug concentration, flow rate and contact time. All the experiments were performed on a laboratory scale set-up by working into static and dynamic regime in order to establish the optimal operational conditions for high removal efficiencies of streptomycin.

2. Materials and Methods

The experiments were carried out using Purolite A-510 anionic exchange resin purchased from Purolite International LTD (UK), their typical properties are listed in Table 1 [9].

Characteristics of resins Table 1

Parameter	**Type A-510**
Matrix	Polystyrene-divinylbenzene
Structure	macroporous
Functional group	$-N^+(CH_3)_2CH_2CH_2OH$
Ionic form	Cl^-
Mean particle diameter/mm	0.64 (±0.03)
Capacity*/meq · g^{-1}	3.93

* determined by *pH*-metric titration of resins dried at room temperature for 72 hours.

The selected drug, *streptomycin* ($C_{21}H_{38}O_{11}N_7$, MW = 564, in form of streptomycin sulphate, commercial product of S.C. Antibiotice S.A. Iaşi), is a biosynthesis antibiotic (i.e. cultivation of Streptomices griseus actinomicette onto a support which contains sources of carbon, organic and inorganic nitrogen, mineral salts, precursors, stimulators) that acts on Koch bacilli, being used in treatment of tuberculosis disease, different septicaemias, endocarditic or pest. The streptomycin was used as commercial salt (streptomycin sulphate, white optical active solids, water soluble, having good thermal stability in dry or solution forms). The drug was used as a stock aqueous solution containing 16 mg/mL. The working solutions were prepared by appropriate dilution of the stock solution with distilled water.

The continuous kinetic experiments were performed by the "column" technique (dynamic regime) or by the "limited bath" technique (static regime). Weighed amounts of anionic resin (10 g) fitted a laboratory glass tubular column (i.e. dimensions of 220 mm-length and 18 mm-diameter) were continuously contacted with different flow rates of streptomycin solution (0.3-1.2 L/h) (i.e. volumes of 500 or 2000 mL with 1.6-16 mg/mL drug). After the predetermined time intervals (i.e. 5, 8, 10 or 12 minutes dependent of flow rate), samples of 1 mL aqueous solution passing over the resin layer were taken for determination of streptomycin content.

Into the "limited bath" technique, 1 g of ion resin was contacted with 25 mL solution containing known amounts of drug, under constant vigorous stirring. All experiments were performed at a constant temperature (room temperature, 293±2 K).

Analysis of drug was carried out by spectrophotometric method with a VIS SP-830 Plus Metertech spectrophotometer ($\lambda = 550$ nm). Each 1 mL sample treated with 1 mL NaOH 0.5N and 5 ml distilled water was heated for 15 minutes, and after cooling 10 mL ferric ammonium alum (solution of 5% into H_2SO_4 4N) was added and absorbance was measured (i.e. violet colour of treated sample).

The regression equation of calibration curve was:

$$A = 0.8046\, C_{drug} + 0.2244\,, \qquad (1)$$

where: A is absorbance at 550 nm in comparison with a blank prepared in the same mode but with 1 mL of distilled water instead of drug solution, and C_{drug} is the calibration concentration of streptomycin (i.e. 0-1.2 mg/mL).

In this study the sorption capacity of the Purolite A-510 anion resin was evaluated by percent of streptomycin removal:

$$R\% = (C_0 - C) \cdot 100/C_0, \qquad (2)$$

where C_0 and C are the initial and equilibrium concentration of drug (mg/L).

In all experiments the tested *pH* was adjusted with HCl or NaOH 0.1N solution and directly measured at a Hach One Laboratory *pH*-meter, Hach Co., USA.

3. Results and Discussion

In our previous works [6-11], the sorption equilibrium of different ionic organic compounds (i.e. dyes) onto Purolite anion exchange resins was studied. The low capacity of resins to remove ionic organic compounds from industrial aqueous effluents has been explained by the inability of large organic molecules to saturate exchange sites of sorbent (the steric hindrance effect). By potentiometric titration of released chloride it was found that immobilization of organic molecule on the studied resins takes place by an ion-exchange mechanism, but also π-π interactions between the organic matrix of sorbent and condensed rings of organic compound [11]. The stoiechiometry of organic compound association with the anion exchange sites is a 1:1 and such relationship is in good agreement with other researchers [13].

In this study the streptomycin sorption onto Purolite resins (A-510) was studied with respect to the following variables: initial drug concentration, *pH* of solution, working regime and solution flow rate.

3.1. Effect of Drug Concentration on Removal Efficiency

- **Working in dynamic regime**

Into the same operational conditions such as: 1 - flow rate of drug solution passing through the anion resin layer of 10 mL/min; 2 - time interval for sampling (1 mL solution after the passing through the column with resin layer inside) of 8 minutes; 3 - *pH* = 5.89, and 4 - room temperature of 293±3 K were performed kinetics of streptomycin sorption onto Purolite A-510 anionic resin. The obtained data were plotted into Figure 1 for different initial drug concentration: 3.2 mg/mL, 6.4 mg/mL, and 9.6 mg/mL respectively.

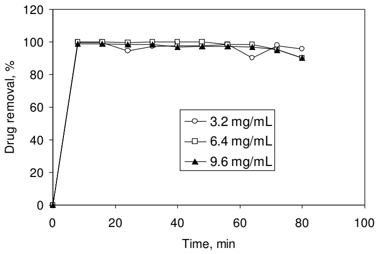

Fig. 1. *Influence of initial drug concentration on ion exchange* (*Purolite A-510*)

As can be seen in Figure 1 the streptomycin removal percentages are very high into the first hour of exchange (i.e. maximum removal of 95.90%, 99.45% and 97.23% respectively). The highest removal was of 99.45% for the initial drug concen-tration of 6.4 mg/mL after 48 minutes, and after 64 minutes the removal was of 90.31% for an initial drug concentration of 3.2 mg/L. It seems that into this concentration range the increasing of drug concentration had no negative influence on the drug removal.

- **Working in static regime**

Into the same operational conditions, the drug solution samples of 25 mL having different initial concentrations of 3.2, 6.4, 9.6, 12.8 and 16 mg/mL streptomycin where in contact ("limited bath" technique) with 1 g Purolite anionic resin. After 24 hours the samples were filtered and analyzed in order to appreciate the drug removal percentage. The obtained data were plotted into Figure 2.

After 24 hours of ion exchange in static regime the drug removals increases up to 98.53%, and can be mentioned that the performed values were approximate constantly.

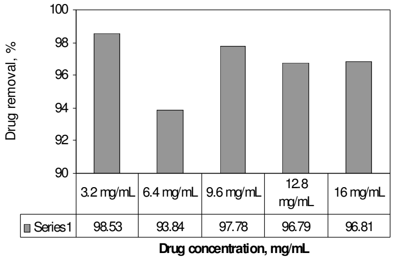

Fig. 2. *Variation of streptomycin removal on Purolite anion exchanger*

3.2. Effect of Solution *pH* on Drug Removal

- **Working in dynamic regime**

Kinetic studies were performed at different *pH* values of initial drug solution and the same operational conditions: flow rate of 10 mL/min, sampling time interval of 8 minutes and temperature of 293±3 K respectively. The experimental results were synthetically presented in Figure 3.

At weakly basic drug solution (i.e. *pH* = 8.56 and *pH* = 10.45 respectively) the drug removals are close enough varying between 81.68-87.75%, but in strong acid drug solution (i.e. *pH* = 3.65) the drug removals were no lower than 72%.

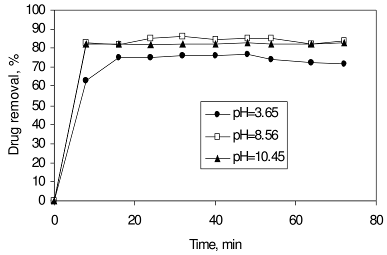

Fig. 3. *The pH effect on drug removal onto Purolite A-510 anionic resin*

- **Working in static regime**

Appling the "limited bath" technique in the same operational conditions for samples of 25 mL streptomycin solution having the initial drug concentration of 12.8 mg/mL treated with 1 g Purolite anion resin but at different initial *pH* values (i.e. *pH* = 2.50, 4.50, 7.0, 9.50 and 11.50) there were obtained experimental data after 24 hours of exchange presented in Figure 4.

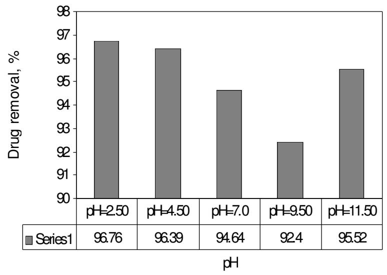

Fig. 4. *The variation of drug removals after 24 hours on Purolite A-510 anion resin vs. pH*

It can be observed that high streptomycin removals were performed into the whole *pH* range of 2.50-11.50 higher up to 92.40%.

3.3. Effect of Solution Flow Rate on Drug Removal

Working in dynamic regime on tubular column having at the bottom an anion resin layer (i.e. resin layer length of 10 cm and resin weight of 10 g respectively), drug solution of 12.80 mg/mL were passed through the resin layer with different flow rates (i.e. 4 mL/min, 10 mL/min, 15 mL/min, 20 mL/min) and samples of 1 mL were collected and analyzed about the streptomycin concentration after an interval period of 5-8 minutes and room temperature (293±3 K). The experimental data resulted in exchange kinetics were plotted in Figure 5.

As was shown in Figure 5 the best results were performed at a low value of drug solution flow rate (i.e. *v* = 5 mL/min) and values of drug removal lower than 50% were obtained after more than 300 min.

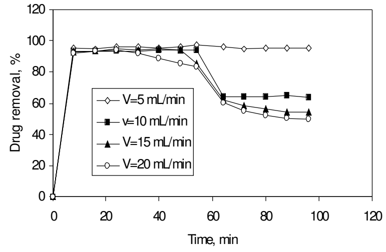

Fig. 5. *The effect of flow rate on drug removals*

Higher solution flow rates were generated constantly decreasing of drug removal (i.e. <50% drug removal) after more that 120 minutes of exchange. The necessity of anionic resin regeneration was appearing after more than 6 hours of continuous working in dynamic regime for the 10 g of used Purolite A-510 resin.

Purolite A-510 anion resin regeneration was made with 100 mL of 10% NaCl solution, after stirring and ion exchange for more than 2 days.

4. Conclusions

- A preliminary study of streptomycin removal from aqueous solutions was performed by a chemical treatment based on ion exchange onto Purolite A-510 anion resin.
- The experiments were made in laboratory conditions of dynamic and static regime in order to understand the effect of some operational variable onto drug removals. In this context, variables concerning the drug quantity (1.6 - 16 g/L), *pH* (3.65 - 10.45), exchange time (0.8 - 5.73 h) and flow rate (0.3 - 1.2 L/h) are considered in order to appreciate the drug removals or treatment efficiency.

- The streptomycin removals using the Purolite A-510 exchanger correspond to values between 62.93 - 96% for different adequate operational conditions for up to 120 minutes of ionic exchange in dynamic regime or 24 hours in static regime.
- The application of Purolite A-510 anionic exchanger to an industrial effluent treatment generated by the technological process of streptomycin production is possible to be applied. The preliminary tests were studied into this paper taking into account the recovery demands of all useful materials (e.g., solvents, antibiotics) and treated wastewater recycling requirements.

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