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論文内容要旨

Chapter I and II General Introduction and Background

The increase of the environmental pollution in aqueous phase with heavy metal ions is a matter of increasing concern, which is reflected in new and more stringent regulations. To meet the new standards, conventional processes for treatment of large volumes of waste waters or industrial effluents having low content of pollutant heavy metal ions have become ineffective and highly cost operations. The generation of sludge, often toxic, resulted in additional shortcomings of some conventional processes. Then, the research for cost-effective alternatives is of primary importance.

The use of solidified alginic acid as a sorbent material for removal of heavy metals is proposed. This acid is a viscous liquid in solution that if used in its natural state resulted in serious problems for separation at the end of the process. The functional group of this acid is the carboxylic one, which has been proved to be effective in reacting with heavy metal ions. Solidification of this acid as beads, alginate beads, results in a sorbent material having potential sorption properties and, furthermore, will permit an easy solid-liquid separation. In addition, the immobilization of a biological entity having functional groups other than the carboxylic one will extend the applicability and potentialities of this sorbent. This will result in a novel sorbent material for environmental control and for recovery of valuable and precious metal ions from low concentrate solutions.

Chapter III Alginate Beads: Production, Properties and Sorbent Potentialities

In this chapter the production of alginate beads, the morphology of the produced beads, their behavior in aqueous solutions and the potentiality as sorbent material of several heavy metals were studied. Reliable alginate beads were obtained by cross-linking alginic acid chains with barium or

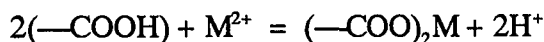
calcium ions, the protocol followed and the optimum conditions for preparation are presented in this chapter. To ensure the complete use of the carboxylic functional group of the formed beads, they were protonated with nitric acid. The morphology of this sorbent material in gel and dry states was analyzed. Gel beads have a perfect spherical shape with a smooth surface. Dried beads presented a distorted spherical shape having a corrugated surface. No morphological differences were found between beads made up with barium or calcium. The diameter of gel beads was 2.8 mm, while for dry beads it was 1.0 mm; both types of beads have a narrow size distribution. Although the dry beads had a rough surface and distorted shape resulting from drying process, this kind of beads was used in the experimental work. The alginate beads were structural and chemical stable in solutions of pH as low as 1.0, however in alkaline environments the beads were seriously deteriorated by a nucleophilic OH β -elimination reaction. Both types of alginate beads have identical behavior in aqueous solutions. The sorption properties of the alginate beads were challenged with different heavy metals (Zn, Cu, Co, Ni and Cr(III)). Significant removal of these heavy metal ions from low concentrate solutions by their uptake in the beads was found. Slightly acidic environments, acid concentration of 1 M for protonation, and ionic strengths lower than 10 mmol/L were found to be the most favorable conditions for the uptake of the heavy metal ions.

Chapter IV Uptake of Divalent Metal Ions Cadmium, Zinc and Copper from Low Concentrate Aqueous Solution

The sorbent property of the Protonated Dry Alginate Beads (PDAB) was systematically evaluated with 3 divalent heavy metals having different chemical properties (Cd, Cu and Zn). Most of the experiments were run in a batchwise system at 25 °C under constant values of pH (ranging from 1.0 to 5.5). The uptake of metal ions increased with the solution's pH up to a value of 4.5 after which it remains constant. At extremely low values of pH (1.0 and 2.0) there was not uptake of any metal ions. The removal of metal ions was coupled with a release of protons; structural Ba or Ca was not liberated from the PDAB during the experiments. The uptake was not affected by the cross-linker (Ba or Ca) used to make the beads. This added to the no uptake at low pH and the no release of cross-linker demonstrated the different nature of the uptake and beads formation mechanisms. The increase of the working temperature favored the uptake between 5 and 25 °C; higher temperatures have no effect on the uptake. Then, no physical adsorption was present during the uptake of heavy metal ions. The metal ions taken up were rapidly stripped back to solution with 0.1 N of HCl, HNO₃ or H₂SO₄, then chemisorption was not present as well. EPMA-EDX analyses made to the cross-section of PDAB after the uptake showed a uniform distribution of those ions throughout the alginate structure. Then, the drying process of the alginate beads generates open pores through which the metal ions can reach the carboxylic functional group of the complete structure of the beads independent of the metal ions and pH of the solutions.

Since the removal of metal ions was coupled to a release of protons, there was not liberation of cross-linker ions and no adsorption was detected, the only mechanism governing the uptake is ion

exchange between protons of the carboxylic functional group of the PDAB and metal ions from the solution. The three heavy metals investigated behave of the same manner; then, the uptake process may be interpreted by the following reaction:



The experimental mole ratio $d[\text{H}^+]/d[\text{M}^{2+}]$ was found to be 2, which was independent of the solution pH. This value demonstrates that a stoichiometric ion exchange mechanism is governing the uptake of the heavy metal ions.

The loading capacity of PDAB for Cd, Zn and Cu was found to be 2.5-2.6 mmol of metal ions per g of alginate beads at pH 4.5. Therefore, based on the behavior of the uptake and the loading capacity, the PDAB is not a metal ion dependent sorbent material, which represents an important feature for a cost-effective process in environmental control.

Figure 1 shows the uptake of Cd, one of the most toxic heavy metals, obtained in this work compared with results recently published in the technical literature for common cationic exchange resins and biological entities. This figure shows the exceptional high uptake achieved by using PDAB as sorbent material. Identical behaviors were observed for the case of the other heavy metals. The residual content of the three heavy metal ions in solution was reduced by the PDAB to levels lower than the standards required for the safety discharge of several types of industrial effluents into the environment.

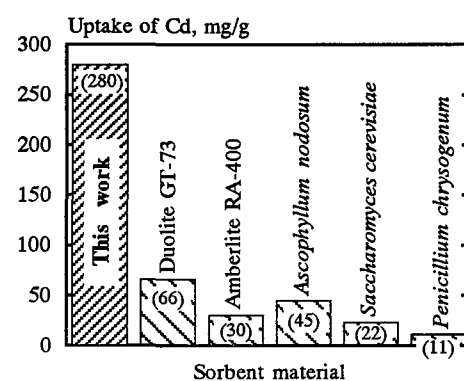


Fig. 1 Comparison of the Cd-uptake between several sorbent materials. Comparison at pH 4.5 and residual concentration of 200 mg/L of Cd.

Chapter V Uptake of Trivalent Chromium Ions from Low Concentrate Aqueous Solutions

The removal of a heavy metal having a complex chemical behavior was studied in this chapter. Trivalent chromium has complex speciation with the pH; it hydrolyzes from Cr^{3+} to CrOH^{2+} and $\text{Cr}(\text{OH})^+_2$ by increasing the solution pH. The removal of this heavy metal by its uptake in the PDAB behaves as described for the divalent heavy metal ions; the uptake increases with the pH until a value of 4.5 after which it may be considered constant. No uptake was observed for pH's lower than 2.0. The simultaneous uptake of chromic species was found to be an ion exchange process between labile protons of the alginate beads and metallic species from the solution. EPMA-EDX analyses showed that the chromic species were uniformly distributed in the entire structure of the beads regardless the pH of the solution, ionic size and contacting time. The loading capacity of PDAB for trivalent chromium was found to be 2.2 mmol/g, which is higher than the values reported in the technical literature for most of the sorbent material. The residual concentration of this heavy metal in solution after contacting with PDAB was lower than the standards requested for the discharge of effluents containing Cr(III).

Chapter VI A Novel Sorbent Material for Environmental Control and Recovery of Precious Metals

The immobilization of a biological entity having functional groups such as NH_2 and SH will raise a novel sorbent material suitable not only to remove cationic species, but also to remove negatively charged complexes such as AuCl_4^- , PtCl_6^{2-} and PdCl_4^{2-} from low concentrate solutions. Egg shell membranes (ESM) were immobilized in PDAB. ESM is made up of an intricate network of randomly oriented proteinic fibers. ESM has NH_2 and SH functional groups, high stability in acidic environments, water-insoluble character and extremely low cost (byproduct). A complete review of this biological entity is given in this chapter. ESM was separated from the calcitic shell after immersion in HCl , then the ESM was cryogenically ground under liquid nitrogen. The particles of ESM were sieved at $300\ \mu\text{m}$; the fine particles were dry and then immobilized in PDAB.

The contact of this novel sorbent material with precious metal ions solutions resulted in a significant uptake of these ions. The uptake increased with the solution pH up to a value of around 4.0; there was almost not uptake at pH 0.5. Experiments with solutions of precious metals having cupric ions proved that there is a selective uptake of the ions. Figure 2 shows EPMA micrographs of the cross-section of a bead after the simultaneous uptake of Pd (A and B) and Cu (C and D). The strong white coloration observed in A and C corresponds to ESM particles. The micrographs show linear (EDX) and mapping (WDX) analysis in A and C, and B and D, respectively. These micrographs show that Pd complexes and cupric ions were selectively taken up by the different constituent of this sorbent. NH_2 and SH groups of ESM did take up Pd while COOH group of the alginate did take up Cu. Identical behavior was observed for platinum and gold.

The selective recovery of Au and Cu was achieved by stripping the sorbent. Cu was recovery first by using H_2SO_4 ; Au was not stripped by this acid. Then, Au was recovered using HCl , both acids having a concentration of 1.0 N.

Therefore, this new sorbent material, based on the immobilization of ESM particles in an alginate matrix, can be considered a cost-effective alternative to be used for environmental control and for selective recovery of valuable and precious metal ions from low concentrate solutions.

Chapter VII General Conclusions

The concluding remarks found during this investigation are summarized in this chapter.

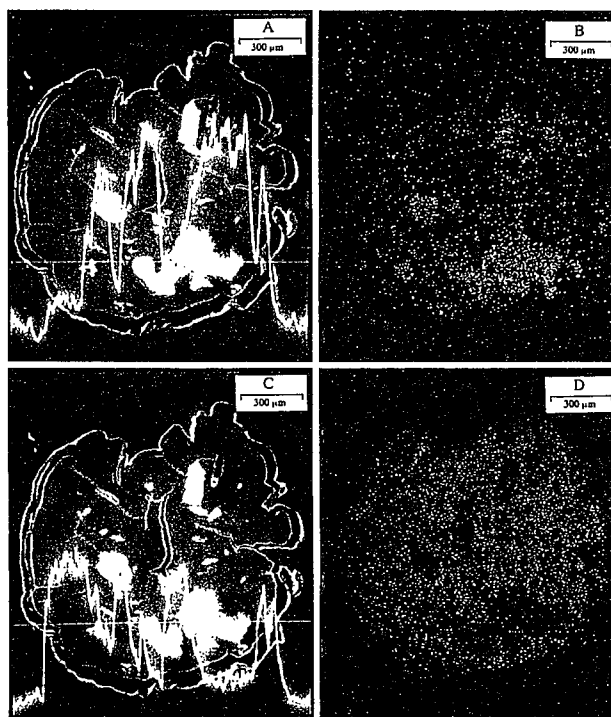


Fig. 2 EPMA micrographs of the cross-section of PDAB showing linear and mapping analyses for Pd (A-B) and Cu (C-D). Metals were selectively taken up; Pd by the ESM and Cu by the alginate matrix.

審査結果の要旨

植物界に広く存在するアルギン酸は、そのアルカリ塩が長い鎖状分子を形成して水に溶け、バリウムあるいはカルシウムイオンに対して分子構造中の酸素原子を配位させ egg box junction を形成して固化する。本研究は、アルギン酸の特性を利用して、微量金属イオン含む排水の処理へのアルギン酸・バリウムビーズの使用の可能性を実験的に示したもので、全編7章からなる。

第1章は総論であり、本研究の背景および目的について述べている。

第2章では、いわゆるバイオマテリアルと水溶液中の金属イオンの反応に関する文献を整理し、本研究の位置づけを明確にしている。

第3章では、アルギン酸塩ビーズの製法を検討し、アルギン酸の固化後もカルボキシル基が活性に保たれ、水溶液中の種々の金属イオンを取り込む機能を有することを見出している。

第4章では水溶液中の低濃度のCu、CdあるいはZnイオンとアルギン酸・バリウムビーズの反応を詳細に追跡した。ビーズに取り込まれる金属イオンと放出される水素イオンの量の間には1対2のモル比が保たれており、イオン交換反応が主反応であることを示し、この主反応に及ぼす溶液側の諸因子の影響を明らかにした。ビーズ内部の目的金属イオンは中心部までほぼ均一に分布し、反応は内部まで迅速に進行していることを明らかにした。これらは、実用を考える上で重要な知見である。

第5章ではCr(III)イオン種とアルギン酸・バリウムビーズの反応をpH 2.0～4.5で追跡している。各pHにおける残留Cr(III)の濃度とCr(III)イオン種の形態を考え合わせ、Cr(III)の除去は、カルボキシル基によるイオン交換が主反応であることを示している。

第6章ではアルギン酸・バリウムのインモビライザーとしての利用について述べている。微粉砕した鶏卵卵殻膜をアルギン酸・バリウムで固化したビーズを用いてAu, Pt, Pd等の塩化物の希薄溶液から貴金属のクロロ錯イオンを卵殻膜に吸収、共存する銅イオンをアルギン酸相に捕捉した。捕集後は酸溶液で選択的に逆抽出が可能であり、低濃度溶液から各金属イオンを分離回収出来る可能性を示した。これは、プロセス排水の処理に関する新しい提言である。

第7章は結論である。

以上要するに本論文は、自然界で得られるアルギン酸をイオン交換体およびインモビライザーとして用いて、廃水中の重金属イオンや有価金属のイオンの回収が可能であることを示したもので、地球工学の発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。