Application of chitosan for the removal of heavy metals from drilling fluids wastewaters

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Abstract. The purpose of this study was to present a possibility of application of chitosan, covalently cross-linked by treating with glutaraldehyde as an effective sorbent of heavy metals ions from drilling wastewaters. The influence of the concentration and pH on the sorption capacity of the modified chitosan was determined in relation to Cr(II), Zn(II), Pb(II) and Cd(II) ions. Sorption parameters were defined. The greatest affinity to the modified chitosan was observed from ions of Zn(II), Pb(II). The effectiveness of the studied process is pH-dependent. Processes of sorption of Cr(II), Zn(II), Pb(II) and Cd(II) ions in the presence of cross-linked with glutaraldehyde chitosan are well-described by Langmuir and Freundlich isotherms, which may be confirmed by high values of correlation coefficients (R>0.91). High values of the maximal sorption capacity (q_0) have been reached for zinc ions (q_0=3.67 mg/g) and lead ions (q_0=3.31 mg/g), calculated on the basis of Langmuir isotherm equation which proves their great affinity to chitosan cross-linked with glutaraldehyde. Obtained results confirm good sorption properties of cross-linked chitosan towards heavy metals and a possibility of application of this sorbent in a wide range of the pH. Even small doses of sorbent, such as 5 g/L, facilitate the effective reduction of Cd, Cr, Pb, Zn content in drilling wastewaters, even from 75 to 90 %. Application of chitosan may be one of alternative and all the same effective methods leading to reduction of the inconvenience of fluid drilling waste.

1. Introduction
It is said that at least twenty metals of all naturally occurring have toxic properties, and a part of those metals is emitted to the environment in a hazardous for human amount [1]. A characteristic feature of heavy metals is their high toxicity, even if not very concentrated; moreover, they have an ability to accumulate in internal organs, which may lead to various disorders and complaints [2]. Taking the aforementioned into consideration, issues concerning the reduction of heavy metals emission to the environment are of significant meaning. Nevertheless, the effective elimination of toxic heavy metals from drilling wastewaters is a rather complex problem, especially bearing in mind the diversity of its composition and properties. Improvements to already coined methods, as well as the development of new technologies in favour of purification of water and wastewaters from heavy metals still remain up-to-date matters. Up to this moment, numerous technologies have been developed, and from those most frequently applied to the elimination of heavy metals in wastewaters shall be chemical precipitation, ion exchange, membrane processes, electrolyte methods, extraction, adsorption [3]. Amidst those, adsorption is considered to be the most versatile and popular, considering its simplicity, low costs, high effectiveness, lack of inconvenient sediments, and a possibility to reuse and regenerate.
sorbents. Being universally applied, activated charcoal is considered to be the most effective sorbent used for the elimination of heavy metals ions, owing to its extensive specific surface area and high sorption capacity. However, it is relatively expensive, and together with a rather complicated process of its separation from wastewaters, both may contribute to its limited usage [4]. Hence, adsorption based on natural resources, especially biopolymers, became a dynamically burgeoning technology, which uses natural adsorbents in the processes of eliminating heavy metals ions from water and wastewaters [5]. There are numerous natural materials, often simply waste, which may be used as an effective sorbent. Serving as natural sorbents in various processes, a wide range of organic materials are used, and above all waste from wood, food, and agricultural industries. For instance, all kinds of fruit and vegetable peelings, sawdust, fruit stones, nuts shells, straw, wood bark, etc. may be used [6,7]. At this point, it is worth mentioning chitin, which right after cellulose is recognised as the most widespread polymers in nature. The estimated annual amount of chitin originating from natural sources reaches approximately 1012 g [8]. High occurrence in the natural environment of chitin, a raw material used for chitosan production, low costs of its production, great sorption capacity with reference to pollutants, such as heavy metals, as well as selectivity and detoxicant properties with reference to solutions with a very low or very high concentration of pollution alike, may be recognised as basic advantages of this sorbent. As a result, using biopolymers such as chitin and chitosan is a dynamically developing sorption method in purifying water and wastewaters from colourants and heavy metals ions, even if the concentration is low [8]. Chitosan is considered to be a perfect biosorbent for the elimination of heavy metals ions, as it does combine unique properties: biodegradation, bioactivity, biocompatibility, and non-toxicity with the fact, that it is the most accessible and inexpensive biopolymer in nature. Its effectiveness has been proved in the elimination of heavy metals ions, such as Cu(II), Zn(II), Fe(III) and Cr(IV) from industrial wastewaters [9]. High affinity of chitosan towards heavy metals is a consequence of a presence of functional groups in its polymer chain, especially –NH₂ and –OH, being able to effectively bind cations of heavy metals, especially when the pH value is approximate to a neutral reaction [10]. Concurrently, this material is prone to impermanence in a low pH, presents insufficient mechanical properties, low thermal resistance, as well as a small specific surface area, and low porosity, which may become obstacles in the transportation of mass [4]. In order to alleviate the aforementioned inadequacies, numerous studies have been conducted on physical or chemical methods of chitosan modification, leading to the introduction of new, improved sorption materials. A physical modification of pulverised chitosan to nano-molecules or gel membranes and balls facilitates mechanical properties, increases porosity and specific surface area, as well as improves diffusion [11]. A solution to a problem of the impermanence of chitosan sorbents in a low pH value shall be a chemical modification through its cross-linking [12]. A process of chitosan cross-linking consists in reaction with a cross-linking factor. In that process, the cross-linking factor creates a bridge between chitosan’s polysaccharide chains, leading to the emergence of three-dimensional mesh. Amongst the most frequently used cross-linking factors for cross-linking of chitosan are dialdehydes, such as glyoxal, formaldehyde, and glutaraldehyde. Cross-linked chitosan remains stable in a wide range of pH, and additionally presents greater mechanical endurance [13]. The cross-linking process also influences sorption properties of chitosan, and its sorption capacity depends on a cross-linking factor and the cross-linking mechanism. The disadvantage of cross-linking is a decrease in the number of free functional groups of amines, as well as in polymer reactivity. Apart from that, the process of cross-linking decreases also accessibility to the interior areas of cross-linked material and leads to a decrease in elasticity of the polymer chain [14]. Whereas this may result in a decrease in sorption capacity of a sorbent, especially if in a reaction of binding pollution functional groups of amines are involved, which are more prone to cross-linking than hydroxyl groups of chitosan. The aforementioned factors indicate the validity of conduction research on assessment of usability one and all modification of chitosan in the process of purification of wastewaters depending on their composition and origin.

Research done on the purpose of the hereby study included a possibility of application of covalently cross-linked chitosan by the use of glutaraldehyde to remove heavy metals ions from
drilling fluids wastewaters. Sorption properties of modified chitosan were examined. The scope of research embraced adsorption of chosen ions of heavy metals from model solutions of zinc, chromium, cadmium, and lead, as well as drilling fluids wastewaters.

2. Materials and methods

2.1. Materials

The research was conducted using the spent drilling fluids from the Miłocino well (Podkarpackie Voivodeship, Poland). The wastes were characterised by a slightly alkaline pH (pH=11). The concentrations of hazardous metals in the considered drilling fluids wastewater was shown in Table 1.

Table 1. Concentrations of heavy metals in drilling fluids wastewater.

| Metal | Concentration [mg/dm³] |
|-------|------------------------|
| Zn    | 11.5                   |
| Cr    | 3.6                    |
| Cd    | 0.42                   |
| Pb    | 0.38                   |

For the purpose of the hereby research, chitosan with molar mass ~200 and deacetylation level >90%, as well as 25% (pure) glutaraldehyde solution of a Polish manufacturer and distributor Pol-Aura, were used. The process of covalent cross-linking of hydrogel balls of chitosan (1mm in diameter) was conducted with glutaraldehyde, according to a commonly used procedure [10]. The amount of cross-linking factor has been chosen in a manner that preserves the number of glutaraldehyde’s functional groups to amine’s functional groups of chitosan in the ratio of 1 to 1.

Tentative solutions of heavy metals from the following salts were prepared: Cr(NO₃)₂·6H₂O, CdCl₂·3H₂O, Ni(NO₃)₂·6H₂O, Pb(NO₃)₂. Concentration of prepared solutions were, for cadmium and lead 0.01 mol/dm³, and for zinc and chromium 0.02 mol/dm³.

Heavy metals content in all research samples was determined via inductively coupled plasma mass spectrometry method in inductively coupled plasma ICP-OES JY 238 Ultrace (Jobin Yvon-Horriba France).

2.2. Influence of pH on sorption of heavy metals ions on chitosan

A row of 100 cm³ plastic bottles containing 1.0 g of cross-linked chitosan sorbent was prepared; then, the samples were poured with distilled water and variable amounts of 0.1 M HCl or NaOH solutions were added. Following a thorough mixing, appropriate volume of the working solution containing 1 mg one of the considered hazardous metals ions (Cd, Pb, Cr, and Zn) was added to each bottle. Afterwards, the content of bottles was topped up to 100 cm³ with demineralised water and the samples prepared in such way were placed on a shaker. After 2 h, the pH of all samples was measured and the concentration of metals in the solution was determined with the ICP method.

2.3. Sorption isotherms

Dependence of the number of heavy metals (Cd, Pb, Cr, Zn) sorbed on chitosan on their equilibrium concentration in water solutions was determined via the static method. To a row of plastic bottles containing 1.0g of modified chitosan 80ml of demineralised water was added, as well as from 1 to 10 ml of a tentative solution of corresponding heavy metal. Then, the pH of the samples was measured, and using diluted solutions of hydrochloric acid, or depending on needs, sodium hydroxide, the pH was adjusted to a level closest approximate to 6, and then the content of bottles was topped up to
100ml. The samples were placed on a shaker and after 24h, the equilibrium concentration of heavy metals in the solution was measured via the ICP method.

The amount of heavy metal absorbed by chitosan was calculated from the difference between the introduced amount and the amount remaining in the state of equilibrium. Similar investigations were conducted for all studied heavy metals, i.e. cadmium, chromium, lead, and zinc.

The obtained data was fitted into Langmuir and Freundlich isotherms [15]. The Langmuir equation has the following form:

$$\frac{c_e}{q_e} = \frac{1}{q_mK_L} + \frac{c_e}{q_m}$$

where: $c_e$ – the equilibrium concentration of metal ions in solution (mg/dm$^3$); $q_e$ – the number of the metal ion sorbed by sorbent mass unit (mg/g); $q_m$ – the maximum amount of ions covering the surface of the sorbent (monolayer capacity) (mg/g); $K_L$ – the Langmuir adsorption constant, characteristics of particular system (dm$^3$/mg).

The essential characteristics of the Langmuir isotherm can be expressed by a separation factor or equilibrium constant $K_R$, which is defined as:

$$K_R = \frac{1}{1+K_Lc_0}$$

where: $K_R$ – dimensionless separation factor; $c_0$ – initial concentration of heavy metal in the solution (mg/dm$^3$); $K_L$ – the Langmuir adsorption constant (dm$^3$/mg).

The separation factor $K_R$ indicates the isotherm shape and whether the adsorption is favorable (0<$K_R$<1) or not ($K_R$>1).Where $K_R$=1 the type of isotherm is linear.

The Freundlich equation is an empirical relationship and has the following formation (R) were calculated with the following formulas:

$$q_e = K_F(c_e)^{\frac{1}{n}}$$

where: $K_F$ is correlated with the quantity of the sorbate associated with the sorbent, and $n$ is the Freundlich isotherm constant related to the strength of the sorption.

The Freundlich exponent, $n$, should have values within the range of 1 to 10 for classification for favourable sorption [15].

2.4. Removal of heavy metals from drilling wastewater
Prepared crosslinked chitosan sorbent in the amounts of 0.1; 0.25; 0.5; 1.0; 1.5; 2.0 g were added to plastic bottles, each containing 100 cm$^3$ of drilling fluids wastewaters. The samples were shaken for 24 h on a horizontal shaker. The experiment was conducted in three parallel repetitions. Then, 10 cm$^3$ of drilling wastes were collected and poured with demineralised water, in line with the PN-EN 12457-2:2006 standard. The samples of water extract were subjected to mineralisation in nitric (V) acid (3 cm$^3$). The mineralisation process lasted for 45 minutes at a temperature of 180 °C and the pressure of 18 bars. The metal ions concentrations were determined with the ICP method.

The adsorption percent (%R) was calculated using the following formula:

$$%R = \frac{c_0-c_e}{c_0} \cdot 100$$

where: %R – adsorption percent; $c_0$ and $c_e$ – concentration of the investigated metal ions before and after extraction.

3. Results and discussion

3.1. Effect of pH
The efficiency of heavy metal ions removal using crosslinked chitosan depending on the pH of the solution, was presented in Figure 1. On the basis of data in Figure 1, it can be stated, that the
efficiency of such removal process using chitosan sorbent was accurately correlated with the value of the sorption’s pH. Reduction of their content in over 50% of all examined heavy metals might have been observed approx. at 4.5 pH. Interestingly enough, as regards lead, the observed level of reduction was evidently higher exceeding 70%. Probably, high degree of lead ions reduction was connected with their largest size among the investigated heavy metal ions and the fact that they were characterised by the strongest physical adsorption by chitosan. Along with an increase in the pH, an increase in the amount of all examined heavy metals sorbed by chitosan was observed. The future increase in the pH, above 6.5 resulted in a slight decrease in cadmium, zinc, and lead removal; and in terms of chromium, that downward tendency occurred only when the pH was near 8.0. Nevertheless, the observed decrease in the effectiveness of the sorption of heavy metals on chitosan was relatively insignificant, as at the level of pH approx. 10 the effectiveness of removal was maintained at the level of 70%. To sum up, it was observed that efficient removal (>90%) of lead and chromium ions occurred at the pH = 5.5÷7, zinc ions – at the pH = 6÷8, while cadmium ions – at the pH = 6.5÷8.

![Figure 1](image1.png)

**Figure 1.** Influence of pH on the degree of metals removal by modified chitosan: a) cadmium and chromium, b) zinc and lead.

### 3.2. Adsorption isotherm

The adsorption isotherms are the basic relations enabling to describe the properties of sorption materials and evaluate their usefulness, which is indispensable while designing adsorption systems. Conducted research on the number of ions of chromium, cadmium, lead, and zinc sorbed on chitosan
cross-linked with glutaraldehyde in a relation to their concentration in water solutions contributed to the development of sorption isotherms, depicted in Figure 2.

![Graphs](image)

**Figure 2.** Adsorption of ions from solution onto natural zeolite fitted to Langmuir (L) and Freundlich (F) isotherm models: a) Cd\(^{2+}\), b) Cr\(^{3+}\), c) Pb\(^{2+}\), d) Zn\(^{2+}\).

The amount of sorbed heavy metals (q\(_e\)), which has been designated experimentally in relation to their equilibrium concentration in the solution (C\(_e\)) was used to develop Langmuir and Freundlich isotherms describing the process of sorption. Constants in mathematical models were designated with the method of least squares via Statistica, using Gauss-Newton estimation method. Besides, applied methods facilitated the determination of the error magnitude of designated constants. The values of parameters for adsorption isotherms of examined heavy metals on natural zeolite are presented in Table 2.

**Table 2.** The values of parameters for Langmuir and Freundlich isotherms.

| Isotherm type | Coefficient | Cd    | Cr    | Pb    | Zn    |
|---------------|-------------|-------|-------|-------|-------|
| Freundlich    | 1/n         | 0.133 | 0.225 | 0.156 | 0.179 |
|               | K\(_F\) (dm\(^3\)/g) | 0.671 | 1.036 | 1.514 | 1.731 |
|               | R           | 0.948 | 0.910 | 0.930 | 0.945 |
| Langmuir      | q\(_m\)     | 1.215 | 2.746 | 3.313 | 3.666 |
|               | K\(_L\) (dm\(^3\)/mg) | 0.371 | 0.218 | 0.180 | 0.486 |
|               | K\(_R\)     | 0.023 | 0.042 | 0.026 | 0.015 |
On the basis of an analysis of acquired experimental data, a conclusion may be drawn, that alongside an increase in the concentration of heavy metals in the solution, their amount adsorbed on cross-linked chitosan sorbent also increase. Those interrelations were of logarithmic character and at that increasing concentration of heavy metal in the solution, a gradual saturation of sorption capacity might have been observed, and measuring points asymptotically approach the maximal value of sorption capacity. Mathematical models used to describe data, namely Freundlich or Langmuir equations, reflected well the course of sorption of chromium, cadmium, lead, and zinc ions from water solutions on cross-linked chitosan. Serving as validation for the aforementioned, obtained correlation coefficients take on values above 0.91. However, undoubtedly better match of the results of heavy metals sorption were found for adsorption isotherms according to the Langmuir equation on the basis of the correlation coefficient. The isotherm constants showed the calculated Freundlich parameters $K_F$ and $n$, which indicated favourable sorption. The values of Langmuir constant $K_L$ for sorption of heavy metals by cross-linked chitosan from 0.180 to 0.486 confirming favourable sorption under the experimental conditions of the study (Table 2).

Maximum sorption capacities $q_m$ (mg/g) calculated from Langmuir model were in most cases comparable with conclusions and results found in the literature on research conducted in similar conditions. [7]. Cross-linked chitosan sorbent used for the purpose of the conducted research, its highest sorption capacity presents for zinc ions, being 3.67 mg/g, and lead ions, 3.31 mg/g. In respect to chromium ions, the maximal value of sorption capacity is relatively high, namely 2.75 mg/g; however, for cadmium ions it decreases reaching only 1.22 mg/g. Notwithstanding, observed interrelation is of minor importance in the whole concept of application of chitosan to eliminate heavy metals from fluid drilling wastewaters on account of extremely low cadmium content.

3.3. Effect of modified chitosan dosage on heavy metal removal from drilling wastes

The adsorbent dose is the main parameter governing the efficiency of metal ions removal through adsorption. Increasing the adsorbent dose ensures better contact surface and greater adsorption capacity. The influence of zeolite dose on the removal of Cd, Cr, Pb, and Zn from drilling fluids wastewaters was presented in Figure 3.

![Figure 3](image_url)

**Figure 3.** Influence of pH on the degree of metals removal by modified chitosan: a) cadmium and chromium, b) zinc and lead.

The effectiveness of the reduction of heavy metals content in drilling wastewaters is inseparably correlated with the amount of applied dose of sorbent (Figure 3). Even minor doses of sorbent, at a level of 0.1 g, contribute to the reduction of chromium and lead ions reaches 65%, and over 50% for
cadmium. In the case of zinc, the reduction reaching only 29% is observed, which most probably is, on the one hand, a consequence of lower affinity of sorbent to zinc ions, on the other of its high concentration in a medium being purified, which results in using up sorption capacity. As a confirmation for observations made may serve results visible with an increase in dosage of sorbent, which rapidly facilitates the effectiveness of zinc ions reduction; while for the other metals increase in reduction is not as spectacular. To all intents and purposes, the maximal level of reduction of the content of cadmium, chromium, lead, and zinc ions is reached when a dosage of cross-linked chitosan applied to wastewaters being purified equals 0.5g. The dose at that level does facilitate a reduction of approximately 75% of zinc and cadmium, concurrently reducing 85% of the content of lead and 90% of chromium. An insignificant improvement in achieved effects of the reduction of heavy metals may be observed applying higher doses of sorbent, yet this kind of approach does not find a practical validation. Moreover, the achievable level of reduction of heavy metals using an optimum dose of chitosan is comparable with the effectiveness of application of other natural sorbents on the basis of food-agricultural waste [16].

4. Conclusions
Chitosan, a product of deacetylation of chitin, the most inexpensive and accessible natural sorbent, owing to a wide range of its chemical and physical modification possibilities arouses great interest in researchers working on new and effective methods of wastewaters purification from colourants and heavy metals. The following conclusions were drawn from the results obtained in the research:
1. Modified chitosan obtained via covalent cross-linking with glutaraldehyde indicated particularly good sorption properties for the reduction of heavy metal ions content in highly polluted solutions.
2. The effectiveness of heavy metals sorption process on cross-linked chitosan depends on the pH of the solution being purified. It was observed that efficient removal (>90%) of lead and chromium ions occurred at the pH=5.5÷7, zinc ions – at the pH=6÷8, while cadmium ions – at the pH=6.5÷8.
3. Sorption on cross-linked chitosan of chromium, cadmium, lead, and zinc ions from water solutions is well reflected in a description of mathematical models of Langmuir and Freundlich. However, better match of the results of heavy metals sorption were found for adsorption isotherms according to the Langmuir equation on the basis of the correlation coefficient.
4. Designated values of maximal sorption capacity of cross-linked by means of glutaraldehyde chitosan are similar for zinc and lead ions and equal 3.67 mg/g and 3.31 mg/g. As regards chromium ions, the value of maximal sorption capacity is lower, being 2.75 mg/g. While for cadmium ions it reaches only 1.22 mg/g.
5. The purpose fullness of applying chitosan for the removal of heavy metals in drilling fluids wastewaters was confirmed. Good removal results were obtained using 0.5 g of chitosan per 100 cm³ of drilling fluids wastewaters. That dose facilitates the reduction of approximately 75% of zinc and cadmium, concurrently reducing 85% of the content of lead and 90% of chromium.

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