



Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Heavy metal removal from industrial effluents by sorption on cross-linked starch: Chemical study and impact on water toxicity

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ARTICLE INFO

Article history:

Received 7 June 2010

Received in revised form

24 September 2010

Accepted 8 October 2010

Available online xxx

Keywords:

Sorption

Metal

Starch

Removal

Industrial effluents

Germination rate

ABSTRACT

Batch sorption experiments using a starch-based sorbent were carried out for the removal of heavy metals present in industrial water discharges. The influence of contact time, mass of sorbent and pollutant load was investigated. Pollutant removal was dependent on the mass of sorbent and contact time, but independent of the contaminant load. The process was uniform, rapid and efficient. Sorption reached equilibrium in 60 min irrespective of the metal considered (e.g. Zn, Pb, Cu, Ni, Fe and Cd), reducing concentrations below those permitted by law. The material also removed residual turbidity and led to a significant decrease in the residual chemical oxygen demand (COD) present in the industrial water discharge. The germination success of lettuce (*Lactuca sativa*) was used as a laboratory indicator of phytotoxicity. The results show that the sorption using a starch-based sorbent as non-conventional material, is a viable alternative for treating industrial wastewaters.

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1. Introduction

Environmental issues, mainly concerning chemical and biological water pollution, represent a key priority for civil society, public authorities and, especially, for the industrial sector. In fact, the use of water, both in urban and industrial contexts, implies its subsequent pollution: any activity, whether domestic, agricultural or industrial, produces effluents containing undesirable, and possibly toxic, pollutants. Thus, a constant effort to protect water resources is being made by the various governments, through the introduction of increasingly strict legislation covering pollutant release. In particular for liquid industrial effluents, recent restrictions impose appropriate treatments of wastewater before its release into the environment.

Of the multitude of industrial activities, surface treatment is one of the largest water consumers and polluters, in spite of the considerable efforts to clean up the effluent made during the last 20 years (Crini and Badot, 2007; Sonune and Ghate, 2004). In fact, surface treatment process water contains both organic and metal

pollution, coming from rinsing and washing baths (Table 1). This high pollutant load poses complex and extremely varied problems, related to each particular situation. In addition, the release of organic and inorganic pollutants is not uniform (either in quality or in quantity), but always leads to the same result: toxicity for aquatic ecosystems which creates worries for the population (Agence de l'Eau, 2002; Blais et al., 1999).

The literature reports a multitude of processes for decontaminating polluted water from surface-treatment industries such as neutralisation, precipitation/co-precipitation, coagulation/flocculation, oxidation/reduction, extraction, evaporation, electrolysis, electrocoagulation, electrodialysis, cementation, ion-exchange, sorption and reverse osmosis (Crini and Badot, 2007; Blais et al., 1999). However, for technological and economic reasons, many of the processes proposed cannot be used on an industrial scale. It is important to note that the surface-treatment sector in Europe is essentially made up of small and medium-sized enterprises (SMEs), which are not very enthusiastic about the idea of investing in additional treatments such as membrane filtration, or electrocoagulation, due not only to their initial high costs, but also to their complicated maintenance (Blais et al., 1999).

In practice, different processes are combined to achieve the desired water quality in the most economic way. A general scheme

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Table 1
Examples of pollution produced by surface-treatment industries.

Pollutant	Origin
Metals	plating, anodising
Cyanides	degreasing, heat-treatment
Organo-halide derivatives	chlorinated oils, degreasing, solvents, paints
Fluorides	cleaning, polishing, passivation
Suspended matter	metal hydroxides
Organic matter	solvents, oils, grease
Nitrogen-containing compounds	cleaning, defatting, etching
Phosphorus-containing compounds	phosphatation, degreasing

of industrial wastewater treatment involves three main successive stages (Crini and Badot, 2007):

- pre-treatment or specific treatment using chemical methods (oxidation, reduction, dechromatation, decyanidation);
- decontamination using conventional physical and chemical methods (neutralisation, precipitation, extraction, flocculation, settling), generally achieved by increasing the pH to convert soluble metals into an insoluble form (e.g. hydroxides);
- treatment of the sludge obtained (e.g. supervised tipping).

Most often it is only these stages that are carried out, but in a few cases, additional treatment (tertiary treatment) can also be required to remove the remaining metal ions and organic load. Conventional technologies such as sorption to activated carbons (ACs) and ion-exchange using polymeric organic resins can be used in the tertiary treatment of wastewaters containing low concentrations of metal ions. Due to their great capacity to sorb pollutants, ACs are the most effective sorbents, and, if the sorption system is properly designed, they give good-quality treated effluent, with concentrations under the legal limits (Dabrowski et al., 2005). However, because of their high cost, sorption to ACs is employed more frequently for the removal of organic compounds rather than metals. Also polymeric resins show excellent complexation abilities, reaching ppb levels in the removal of metals. However, ion-exchange is non-selective and highly sensitive to the solution pH. Moreover, the widespread use of these techniques is also restricted because of their high cost. For these reasons, such treatments are unsuitable (Blais et al., 1999) for most companies involved in surface finishing, and particularly SMEs. Thus, to avoid these problems, many attempts have been made to find inexpensive alternative sorbents that are effective and acceptable for industrial use.

A large variety of non-conventional sorbents such as agricultural waste, sawdust, bark, industrial by-products, clays, zeolites, peat, biomass, biopolymers, etc. have been proposed and studied for their ability to remove pollutants including heavy metals (Monash and Pugazhenth, 2009; O'Connell et al., 2008; Oliveira and Franca, 2008; Qu, 2008; Li et al., 2008a; Dias et al., 2007; Lodeiro et al., 2006; Crini, 2006a; Volesky, 2001; Kratochvil and Volesky, 1998; Veglio and Beolchini, 1997). Among biopolymers, much attention has recently been focused on starch-based materials (Crini, 2005).

Cross-linked starch-based sorbents represent an important class of starch derivatives. They are formed covalently by cross-linking the polymer itself by means of cross-linking agents, and have a three-dimensional network structure which can swell in aqueous medium without dissolving (Crini, 2005). Li et al. (2008b) showed that the sorption of Cu^{2+} , Co^{2+} and Ni^{2+} to cross-linked starch microspheres occurs efficiently in a few minutes and over a wide range of temperatures. Guo et al. (2006) and Xing et al. (2006) also demonstrated the usefulness of starch-based materials for the removal of various metal ions present in industrial wastewaters. As a breakthrough in their utilization, chemical derivatization onto polymer

chains has also been proposed to produce ion-exchanger materials. Amphoteric starches with carboxymethyl and quaternary ammonium groups have been investigated by Xu et al. (2005, 2004) as sorbents for the efficient removal of Cu^{2+} and Pb^{2+} in solution. In previous papers (Crini, 2006a,b; Gimbert et al., 2008; Renault et al., 2008), we proposed the use of these materials as new sorbents for the removal of dyes and aromatic compounds, with interesting sorption properties.

Pursuing our studies of such materials, here we report their use for the sorption of heavy metals present in industrial water discharge. The effects of operating variables (i.e., mass of sorbent, contact time and pollutant load) on the percentage removal were evaluated using the batch method. The germination rate of lettuce (*Lactuca sativa*) was used as a laboratory indicator of phytotoxicity. Toxicity tests were carried out by applying a standard test to discharged industrial waters and to the same discharged waters after sorption treatment.

2. Materials and methods

2.1. Sorbent

The starch from flour (Sauvin SA, Patornay, France) was cross-linked using 1,4-butanediol diglycidylether as cross-linking agent in presence of NH_4OH and 2,3-epoxy-propyltrimethylammonium chloride, and then it was carboxymethylated by means of a chloroacetic acid solution (all chemicals were purchased from Aldrich, France) as described elsewhere (Renault et al., 2008; Gimbert et al., 2008). The polymer characteristics are: particle size 150–250 μm , BET surface area 70 $\text{m}^2 \text{g}^{-1}$, N(%) 4 and DS (degree of substitution in carboxymethyl groups) 0.2.

2.2. Industrial effluents

Industrial effluents were collected from Zindel Industry, located in Devecey (Doubs, France), whose wastewater treatment plant, typical of SMEs, is shown in Fig. 1. The analytical characteristics of 19 samples (taken on 19 consecutive days) are shown in Table 2. The final pollutant load was compared to the limits allowed by local authorities (Agence de l'Eau, 2002). For a flow of 8 $\text{m}^3 \text{h}^{-1}$, discharge standards should be below 300 mg L^{-1} for the COD, 5 mg L^{-1} for Fe, 3 mg L^{-1} for Zn, 2 mg L^{-1} for Cu, 2000 $\mu\text{g L}^{-1}$ for Ni, 500 $\mu\text{g L}^{-1}$ for Pb, and 200 $\mu\text{g L}^{-1}$ for Cd.

2.3. Analytical methods

The physicochemical characteristics of the effluents were monitored through daily sampling and analysis. The following parameters were measured: turbidity, COD, pH and heavy metal content of the solution. Samples for measurements were collected in 3 L plastic bottles and transported to laboratory for analysis. The turbidity was measured in triplicate using an Aqualytic turbidimeter (PCCcompact, Dortmund, Germany) at 875 nm and the results are reported in nephelometric turbidity units (NTU). COD was determined by the dichromate COD method based on the use of colorimetric measurement for high-range COD (0–1500 mg L^{-1} range) using potassium hydrogen phthalate solutions as standards. Samples and standards were placed on a preheated COD reactor (model FB15006, Fisher Bioblock Scientific, Illkirch, France) for 2 h at 148 °C. Following incubation, the absorbance was measured at 605 nm using a photometer (model COD Vaxio, Aqualytic PCCcompact, Dortmund, Germany). The pH of each sample was measured using a portable pH meter (3110 model, WTW, Alès, France).

Metal concentrations in the effluent (Pb, Cd and Ni) were measured in triplicate by means of a furnace atomic absorption spectrometer (Zeeman Correction, Varian models 240Z, Les Ulis,

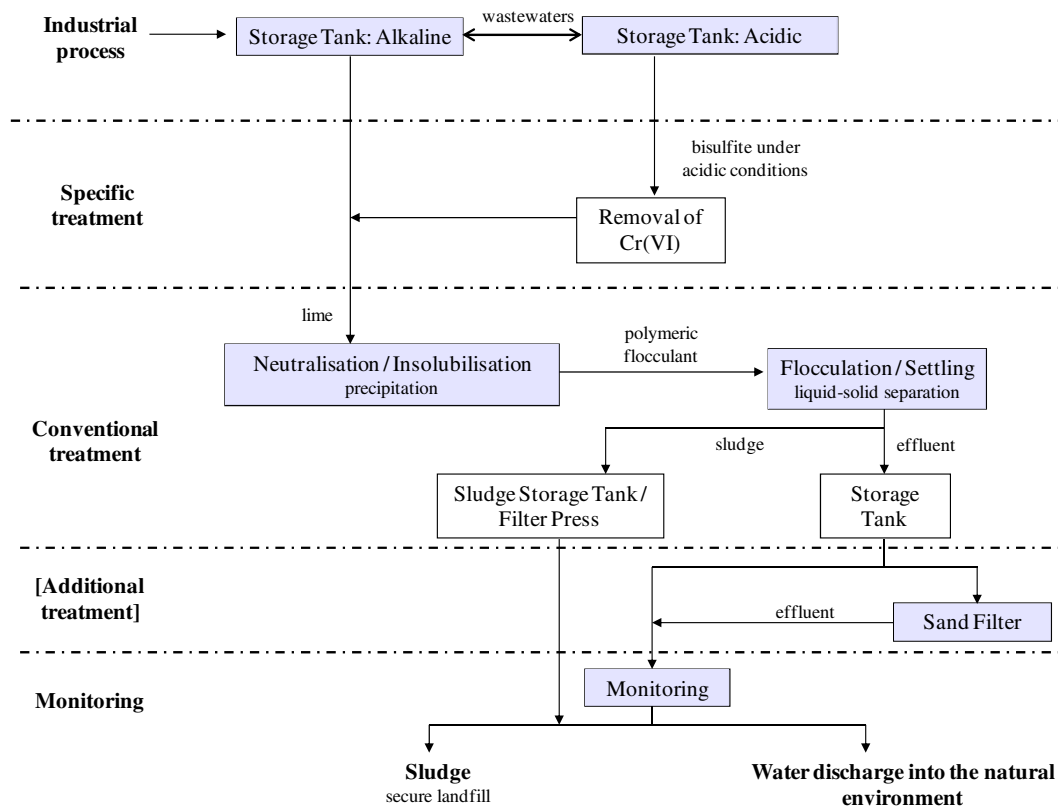


Fig. 1. Physicochemical treatment plant used at Zindel Industry for metal removal from industrial effluents (Devecey, Doubs, France).

France). The accuracy of the analytical methods was checked with respect to standard reference materials (matrix reference ERM-CA011a, LGC Promochem, Molsheim, France). For lead determination, an ultra-lamp was used to increase the sensitivity, regularly including blanks and reference samples during the procedure. Calibration with appropriate solutions, prepared from a $1000 \mu\text{g mL}^{-1}$ aqueous standard stock solution (Fisher Scientific Bioblock, Illkirch, France), was successfully used for the measurements. Results were expressed in $\mu\text{g L}^{-1}$. On the other hand, Zn, Cu and Fe concentrations in the effluents were measured by a photometer (Spectroflex 6100 portable model, WTW, Alès, France) using rapid test kits (cuvette test and/or reagents test). Results are expressed in mg L^{-1} .

2.4. Batch experiments

The experiments were conducted using the batch method without changing the solution pH (8–9, see Table 2) in order to simulate the industrial process. In each experiment, 100 mg of sorbent were mixed with 100 mL of treated wastewater (industrial discharge) in a tightly closed flask. The solution was mixed on a thermostatic mechanical shaker operating at 300 rpm at room temperature ($22 \pm 1 \text{ }^\circ\text{C}$). The solution was then filtered, or centrifuged, and analysed. Contact time and mass of sorbent were varied to investigate their effects on pollutant removal. Each experiment was conducted in triplicate under identical conditions to confirm the results (experimental error within 3%). The sorption performance, representing the ratio between the amount of adsorbed pollutant and the starting amount of pollutant, is expressed in percentage uptake.

2.5. Germination of lettuce seed

Seeds of lettuce (*L. sativa*) were purchased from *Sélection Laitue* (Aramon, Gard, France). They were kept in a dry dark place under

room temperature before use. Experiments based on seed germination were conducted using the French normalized method AFNOR NF X 31-201: ten seeds were placed on two filter paper disks in Petri dishes ($100 \text{ mm} \times 15 \text{ mm}$), and 4 mL of water solution (e.g. control, industrial water discharge and water discharge after treatment by biosorption) was added every two days. Petri dishes were taped and seeds were germinated in a growth chamber under controlled conditions (air temperature $24 \text{ }^\circ\text{C}$, dark). Seed germination success, expressed as the ratio of the number of germinated seeds to the number of seeds sown, (average of three replications for each solution), was evaluated after 10 days. Then, the Wilcoxon statistical test was applied to compare the results obtained (Wilcoxon, 1947).

3. Results and discussion

3.1. The physicochemical treatment of Zindel's wastewater

The Zindel surface-treatment industry (Devecey, Doubs, France) uses large volumes of water, generating similar volumes of raw wastewater ($\sim 8 \text{ m}^3 \text{ h}^{-1}$), processed by the treatment plant described in Fig. 1. The treatment involves two main steps: after a specific pre-treatment for Cr(VI) removal, the wastewater is neutralised using hydrated lime as chemical agent to precipitate the metal ions; then, the effluent is flocculated using an anionic polymer followed by a decantation step (settling time = 2–3 h) before discharge into the aquatic environment. Precipitation is both cost effective and efficient, but it is pH-dependent and affected by the presence of other ions, organic compounds and salts. In addition, precipitation with lime lacks specificity and does not reach very low concentrations of metal ions (ppb level).

Sometimes, before discharge, an additional tertiary treatment is necessary to remove residual suspended solids (SS). Generally, this is achieved by a filtration step using sand filters (Fig. 1), which is

Table 2
Physicochemical parameters of effluent collected over 19 days from Zindel's (Devecey, Doubs, France) treatment plant (pH measured at 20 °C ± 0.1).

Day	pH			Turbidity (NTU)			COD (mg L ⁻¹)		
	Raw wastewater	Treated water for discharge	Water for discharge treated by adsorption	Raw wastewater	Treated water for discharge	Water for discharge treated by adsorption	Raw wastewater	Treated water for discharge	Water for discharge treated by adsorption
1	7.9	8.2	7.2	545	18	16	1300	103	56
2	8.7	8.5	7.4	733	21	7	890	89	6
3	8.6	8.3	7.2	827	23	16	518	97	34
4	8.0	8.7	7.9	1303	17	13	931	67	21
5	9.0	8.3	7.9	978	19	15	1183	93	22
6	8.5	8.0	7.2	1298	9	4	758	51	19
7	8.9	8.6	7.7	675	23	8	889	156	44
8	9.1	8.8	8.1	1024	31	18	1039	125	49
9	8.2	7.9	7.0	1257	15	10	911	87	31
10	8.8	8.3	7.6	1039	19	7	923	176	67
11	8.7	8.4	7.2	987	14	5	798	109	56
12	8.6	8.2	7.1	799	20	9	699	251	68
13	9.1	8.2	7.7	703	13	9	539	108	38
14	8.7	8.3	7.2	679	11	6	602	94	51
15	8.5	8.1	6.9	605	23	13	1021	119	62
16	8.1	8.3	7.4	1451	30	18	1739	263	81
17	8.8	8.2	7.2	1398	26	16	1523	182	50
18	8.6	8.0	7.5	737	17	8	823	69	29
19	8.9	8.6	7.5	821	27	11	1103	131	77

Day	Zn (mg L ⁻¹)			Fe (mg L ⁻¹)			Cu (mg L ⁻¹)		
	Raw wastewater	Treated water for discharge	Water for discharge treated by adsorption	Raw wastewater	Treated water for discharge	Water for discharge treated by adsorption	Raw wastewater	Treated water for discharge	Water for discharge treated by adsorption
1	5.32	4.3	2.4	1.89	0.81	0.11	0.121	0.099	0
2	7.91	2.51	1.22	2.03	0.73	0.04	0.106	0.077	0
3	7.45	2.85	0.08	1.99	0.66	0.10	0.097	0.062	0.011
4	8.23	2.97	1.48	1.36	0.54	0.05	0.089	0.051	0
5	6.82	1.38	0.32	1.56	0.39	0.04	0.090	0.055	0
6	10.2	3.21	1.07	2.22	0.97	0.27	0.105	0.087	0
7	11.25	5.13	2.29	1.95	0.80	0.19	0.113	0.091	0.021
8	12.34	1.13	0.22	1.89	0.71	0.04	0.330	0.120	0.019
9	7.25	2.98	0.23	1.42	0.63	0.09	0.045	0.013	0.001
10	13.2	6.99	3.13	1.66	0.71	0.33	0.065	0.015	0.005
11	6.33	2.41	0.08	0.71	0.34	0.09	0.124	0.090	0.003
12	19.8	10.5	4.77	2.56	1.20	0.44	0.045	0.020	0
13	8.44	1.57	0.29	3.17	0.86	0.09	0.590	0.290	0.039
14	8.51	3.28	1.07	1.33	0.60	0.10	0.350	0.210	0.018
15	9.23	3.71	2.02	1.11	0.52	0.15	0.102	0.080	0
16	51.3	7.31	1.31	4.49	2.30	0.51	0.520	0.310	0.061
17	31.7	2.98	0.61	6.65	2.70	0.66	0.610	0.280	0.076
18	9.89	1.41	0.17	3.31	1.09	0.05	0.210	0.037	0
19	15.9	4.85	0.58	1.01	0.47	0.13	0.099	0.060	0

Day	Pb (µg L ⁻¹)			Cd (µg L ⁻¹)			Ni (µg L ⁻¹)		
	Raw wastewater	Treated water for discharge	Water for discharge treated by adsorption	Raw wastewater	Treated water for discharge	Water for discharge treated by adsorption	Raw wastewater	Treated water for discharge	Water for discharge treated by adsorption
1	11.90	9.67	4.12	0.341	0.29	0.091	387	344.6	159.1
2	9.90	7.20	3.01	2.39	2.1	0.921	345	321.5	145
3	10.20	6.80	2.61	0.76	0.51	0.220	371	313	139.2
4	9.10	4.30	2.18	2.13	1.91	0.310	402	297	121.7
5	10.91	5.21	3.11	3.19	2.77	0.510	506	387	109
6	13.10	9.40	5.01	0.99	0.77	0.130	703	661.2	289.9
7	4.20	3.30	1.67	4.10	3.70	1.020	623	589.2	301.6
8	7.83	3.98	1.72	3.88	2.11	0.360	709	599.4	127.9
9	5.30	4.31	1.03	3.49	3.10	0.570	846	810.9	396.6
10	7.01	5.93	2.41	6.31	5.20	2.010	699	641.3	297.7
11	9.87	8.77	3.05	0.87	0.57	0.080	303	253.1	110.8
12	3.20	2.42	1.12	0.66	0.29	0.071	326	235.4	108.4
13	6.92	3.56	1.22	1.79	1.08	0.098	363	202	97.8
14	13.3	10.0	3.61	1.98	1.10	0.095	407	340	92.5
15	3.80	2.97	1.43	1.34	0.87	0.088	344	331.6	87.2
16	17.90	15.10	3.38	5.91	3.97	2.180	1039	709	406
17	14.82	9.57	4.12	4.09	2.95	1.820	1153	865	503
18	7.71	4.38	1.61	1.71	0.79	0.150	402	302	131
19	5.90	4.80	1.34	2.01	1.33	0.110	939	775	108.9

efficient, until clogging occurs, which is often the case. Filters must be run in duplex (i.e., while one filter is being used for filtration the other one is being washed) to limit clogging, implying regular and optimal filter washing. These problems rebutting industrial users, it

is necessary to optimize the process and/or to find new alternatives to achieve the ever more stringent limits of the law.

Sampling both the raw wastewaters and the discharged waters for 19 consecutive days produced a survey of the physicochemical

characteristics of Zindel's effluents. Discharged waters were treated by sorption on starch-based material and their physicochemical parameters were studied. Table 2 reports the pH, turbidity, organic load (COD) and heavy metal levels (main ions are Zn, Fe, Cu, Ni, Pb and Cd) for all three effluent types.

The raw wastewater was highly polluted, the degree of pollution presenting marked changes over the study period, evidently depending on the processes being applied at a given time. The COD and turbidity values were in the range of 500–1750 mg O₂ L⁻¹ and 550–1500 NTU, respectively, while the pH of the raw effluent always remained between 8 and 9 (± 0.1). A detailed analysis of the dissolved cations indicated the presence of Zn (5–50 mg L⁻¹), Fe (0.7–6.7 mg L⁻¹), Cu (0.04–0.6 mg L⁻¹), Ni (300–1150 μ g L⁻¹), Pb (3.2–17.9 μ g L⁻¹), and Cd (0.3–6.3 μ g L⁻¹). The physicochemical treatment used at Zindel lowered COD by 80–90%, turbidity by 95–98%, Zn by 20–90%, Fe by 50–70%, Cu by 20–90%, Ni by 10–30%, Pb by 20–40%, and Cd by 10–30%. The standard discharge limits (see section 2.2) are respected, except in some cases (e.g. effluents 10, 12 and 16) for zinc, implying for Zindel the necessity of an additional storage tank for subsequent effluent recycling in the treatment plant.

3.2. Pollution removal by sorption on starch material

3.2.1. Batch studies

Batch methods are widely reported to describe the sorption capacity and performance of the process (Crini, 2005). Simplicity, well-established experimental methods, and easily interpretable results are some of the most important reasons frequently evoked for the extensive usage of these methods. Besides, in batch systems, the solution parameters, such as mass of sorbent and contact time, can be controlled and/or adjusted, leading to the improvement of the process.

Water discharged from Zindel's treatment plant (Fig. 1) was subjected to a further sorption step on a cross-linked starch-based material using the batch method to improve residual pollution removal.

3.2.2. Influence of contact time

Fig. 2 shows the sorption performance, expressed as pollutant removal (in percentage) of starch-based sorbent versus contact time

(in minutes) toward the six metals (Cu, Fe, Cd, Ni, Zn and Pb) present in sample 4. To compare the sorption behaviour of metals, the mass of sorbent was kept constant and removal monitored by detecting the metals remaining in solution in the supernatant with the procedure described in the previous section. The short time of only 60 min necessary to reach the plateau, for all the metals, besides indicating strong interactions between metals and the polymer network, suggests all the metals have a similar affinity for the starch surface (Fig. 2). The affinity between the sorbent and the adsorbate is the main interaction force controlling sorption. Crini and Badot (2010) previously reported that the sorption mechanisms are complex because a large number of interactions, such as ion-exchange, physisorption, hydrogen bonding and hydrophobic interactions, are involved. In Fig. 2, it can be seen that pollutant removal rapidly increases due to fast interactions between metals and the surface of the material, and keeps increasing gradually until equilibrium is reached and then remains constant. These experimental results suggest that 60 min is sufficient to reach sorption equilibrium for all six metals present in sample 2. The Cu, Fe and Cd content (except for some samples, with regards to cadmium) showed very high removal efficiency, while the amount of Ni, Zn and Pb was only halved, though the regulation limits were always respected. Kinetic measurements showed that the process is rapid and uniform: the time profile of metal uptake is a single, smooth, continuous curve leading to saturation. At a constant starch:solution ratio of 1/1000 (w/v), similar trends were found for the other effluents, confirming that 60 min is sufficient to reach the equilibrium state, independently of the initial metal concentration of the effluent.

3.2.3. Influence of sorbent mass

Metal sorption on starch-based material was studied by changing the amount of sorbent added to sample 4, taken as model effluent in this experiment in order to keep the concentration of the six metals constant (Cu, Fe, Cd, Ni, Zn and Pb), and fixing the contact time (60 min), speed and pH (8–9, without modification to replicate the industrial conditions). The results (Fig. 3) show that the percentage of metal removal increased with the mass of sorbent reaching equilibrium when 0.1 g of sorbent was added. As expected, this overall trend corresponds to the increase of the interactions between adsorbing material and metals. This behaviour is ascribable

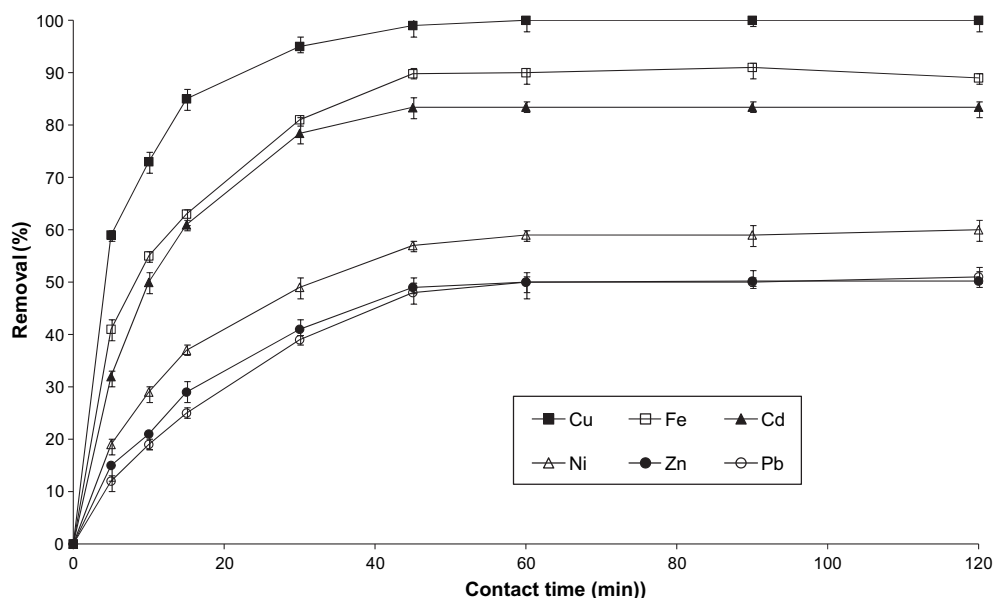


Fig. 2. Influence of contact time on the % removal of metal (Cu, Fe, Cd, Ni, Zn and Pb) by starch-based sorbent (conditions: effluent 4, sorbent mass 100 mg, volume of the solution 100 mL, temperature 22 °C).

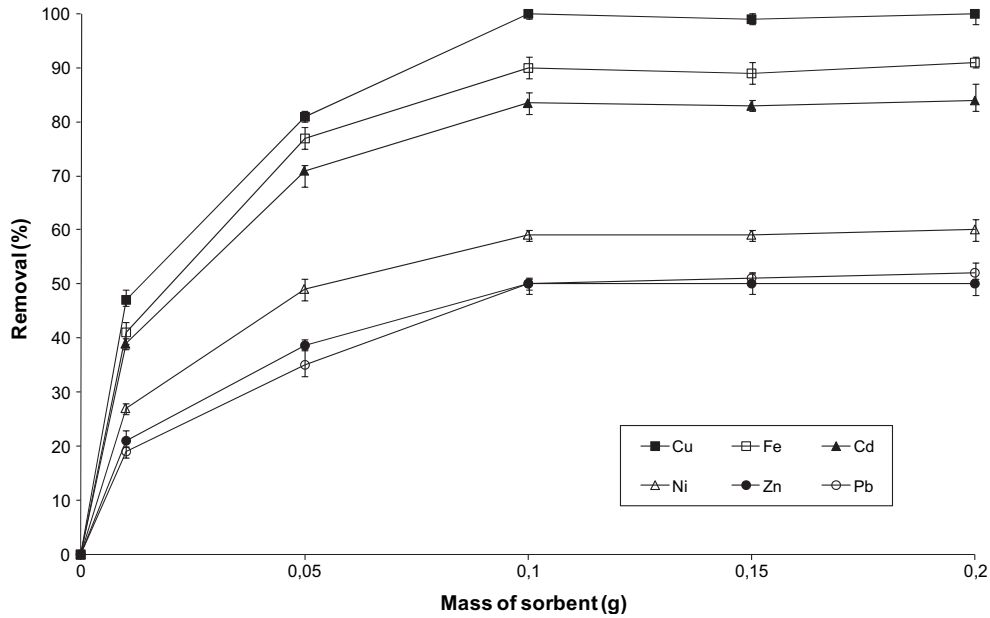


Fig. 3. Effect of sorbent mass on the % removal of metal (Cu, Fe, Cd, Ni, Zn and Pb) by starch-based sorbent (conditions: effluent 4, contact time 1 h, volume of the solution 100 mL, temperature 22 °C).

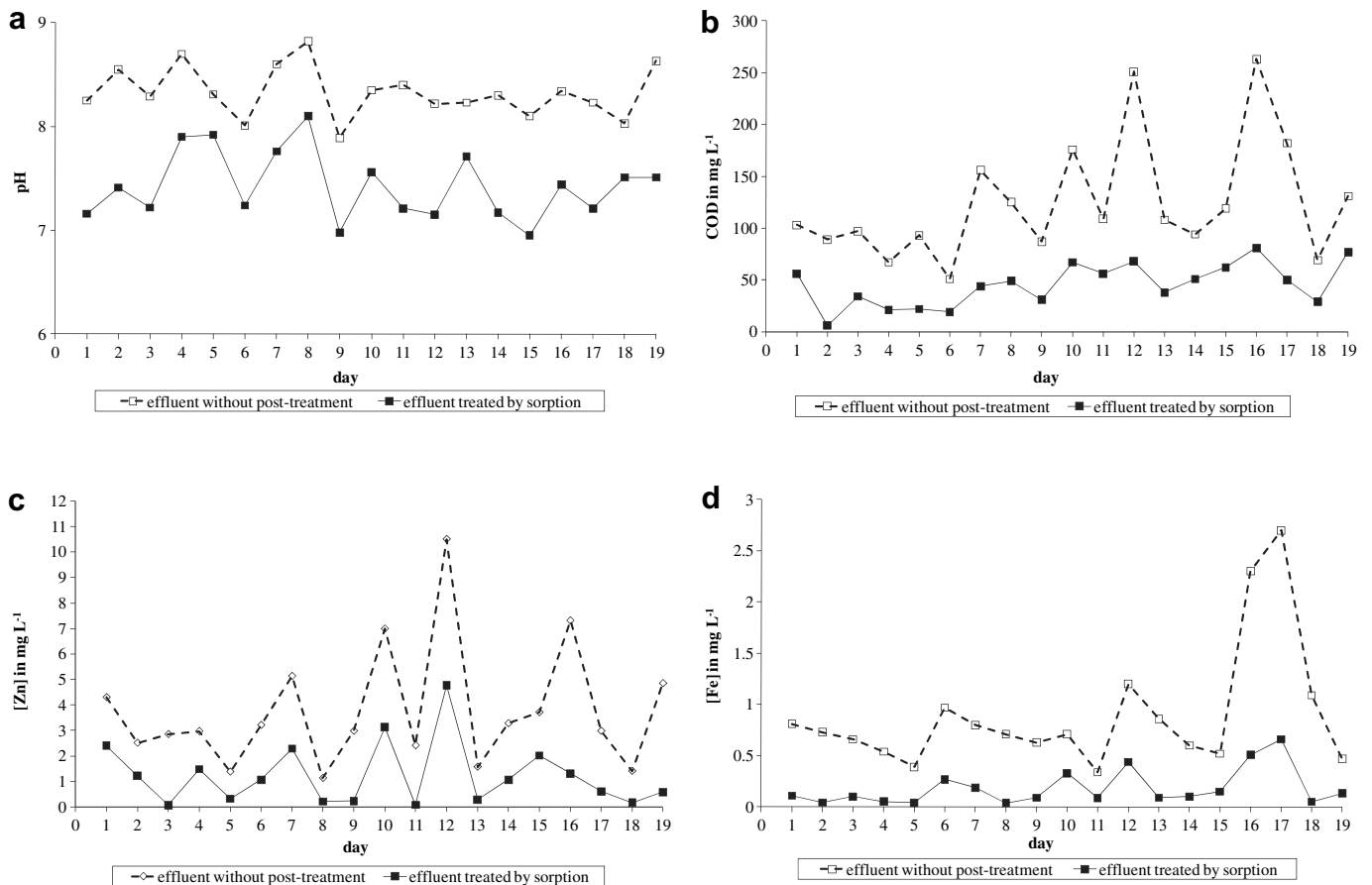


Fig. 4. Effect of sorption onto starch-based sorbent on a) pH, b) COD, c) [Zn] and d) [Fe] for discharged effluents. Comparison between water discharged in the natural environment without additional post-treatment (dotted lines and empty symbols) and the same water treated by sorption (full lines and symbols).

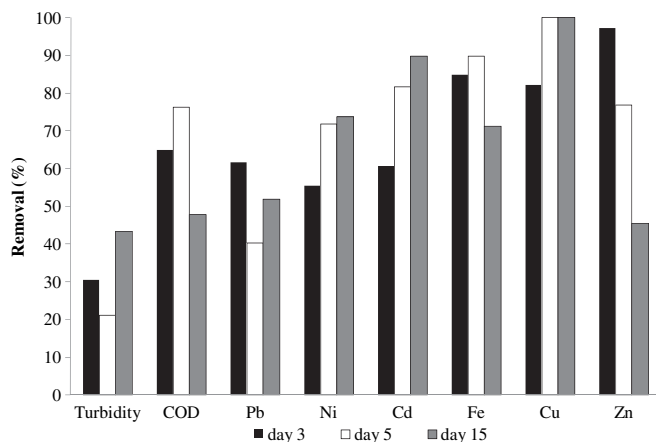


Fig. 5. Additional removal provided by sorption on three treated effluents.

to the higher sorbent surface area and thus the active sites available. For the other effluents, similar trends were found for both the curves and the results.

3.2.4. Overall performance of sorption

In Table 2 physicochemical parameters (turbidity, COD and metal concentrations) of industrial water discharged into the natural environment and the same discharged water treated by sorption, sampled over 19 consecutive days, are summarized. The data demonstrate significant removal for the colloidal organic and metal pollution for each effluent treated by sorption, with a strong decrease of the different metal concentrations. For zinc, the values fell below the regulation limits for discharge (3 mg L^{-1}), except for samples 10 and 12, which already presented a high load of the metal. For samples 3 and 11, the sorption treatment led to quasi complete elimination of both the organic and the metal pollution. The sorption lowered COD by 40–50%, turbidity by 60–70%, and metals by 70–100%. In particular, Cu and Fe almost completely disappeared in all samples after the sorption treatment. These results are visually confirmed in Fig. 4 for COD, Zn and Fe. Moreover, sorption on cross-linked starch decreased the pH by one unit, avoiding excessive alkalisation of the natural environment by the effluent.

Fig. 5 gives further evidence of the benefit of the sorption treatment for all the parameters investigated. It points out the dependence of the removal performance on the composition of the

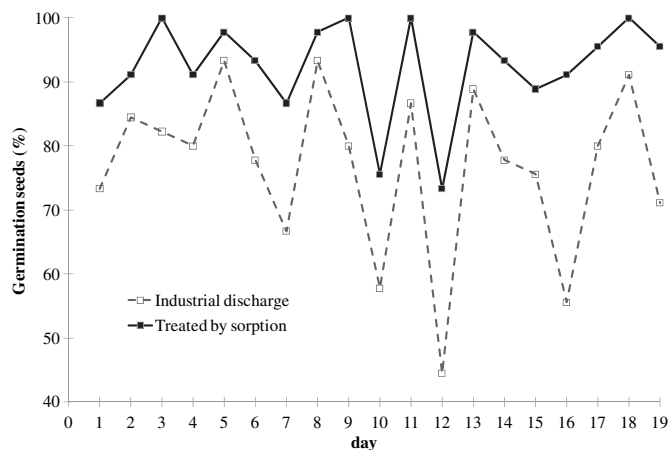


Fig. 6. Comparison of the germination success of *Lactuca sativa* seeds soaked in industrial effluent (dotted lines and empty symbols) and the same effluent treated by sorption (full lines and symbols).

effluent. In fact, it is difficult to link the abatement of each parameter with the initial composition, since the removal order reported in paragraph 3.2.2 for the six metals is sometimes not constant. Further experiments are in progress to understand this phenomenon better.

3.3. Toxicity tests on *L. sativa*

Effluent treated by sorption, or not, was subjected to germination tests with *L. sativa* seeds using the normalized method described in the experimental section. Fig. 6 shows that 19 samples, with the chemical composition reported in Table 2, had different effects on the germination rate. In fact, for the industrial discharged water, a decrease of the germination rate of about 30% was observed, with the decrease depending on the different effluents. The inhibition can be caused by the varying concentrations in organic and metal load. After sorption, the impact on lettuce germination was significantly reduced, reaching almost 100% germination success (p -values = 7.744×10^{-6}). There was a significant difference (Wilcoxon's test) between the effects of the two kinds of water. Metal removal by the sorption treatment obviously decreased the water toxicity allowing the germination of almost all the seeds. Thus, sorption on starch represents an interesting tool for preventing or decreasing the environmental impact of industrial effluent.

4. Conclusions

In this work, we studied the sorption of heavy metals from industrial effluent onto a cross-linked starch-based sorbent. The results showed that this material can be effectively used as a sorbent for metal and organic pollution removal. Experimental data indicated that the removal performance was dependent on operating variables such as mass of sorbent and contact time, and the process was rapid. The sorbent also removed residual turbidity and led to a significant decrease in the residual chemical oxygen demand. Metal load was also significantly decreased with almost complete removal of Cu and Fe, a useful decline of Pb, Cd and Ni, and an abatement of the Zn content to under the legally required limit. In addition, germination tests confirmed the efficiency of the sorption to radically decrease the effluent toxicity. This sorption process proved efficient for the treatment of industrial effluents containing complex mixtures of pollutants both qualitatively and quantitatively, suggesting that experiments should now be carried out at the pilot scale to investigate the feasibility of its implementation on an industrial scale.

Acknowledgements

Authors thank the Agence de l'Eau Rhône-Méditerranée-Corse for financial support (METALDEX Program - Development of Biosorbents for Metal Removal). The research grants given by the CNRS, the University of Franche-Comté and the Conseil Régional de Franche-Comté, which provided financial support for the Ph.D. students B. Sancey and J. Charles, and the post-doctoral researcher G. Trunfio, are gratefully acknowledged. The authors also thank Dr. Nadia Morin-Crini (University of Franche-Comté, UMR Chrono-environnement, Besançon, France) for helpful discussions.

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