Water Purification by Sulfide-Containing Activated Carbon

Franz D. Oeste¹, Rainer Haas², Lothar Kaminski³

¹gm-Ingenieurbüro, Tannenweg 2, D- 35274 Kirchhain, Germany ²Büro für Altlastenerkundung und Umweltforschung, Stadtwaldstraße 45a, D-35037 Marburg, Germany ³Institut für Immunologie, Bereich Umwelthygiene, Pilgrimstein 2, D-35037 Marburg, Germany

Corresponding author: Dipl.-Ing. Franz D. Oeste

Abstract

We investigated a new kind of activated carbon named **gaiasafe-Formstoff** [1] as an agent for powerful heavy metal reduction. This activated carbon contains highly dispersed sulfide compounds. Our investigations with lead containing wastewaters showed an outstanding metal sulfide precipitation power of the new agent. The lead reduction rates are independent of wastewater parameters like lead concentration and complexing agent concentration. Contacted as powder or as a fixed bed with wastewater: gaiasafe-Formstoff showed the best cleaning capacity in comparison to all other agents tested. Investigations with gaiasafe-Formstoff about its ability to reduce the contents of further heavy metals in wastewater are under way. The gaiasafe-Formstoff reaction products with wastewater represent an energy-rich and raw material-rich resource when fed to metallurgical processes.

Keywords: Activated carbon; gaiasafe-Formstoff; lead; residue recycling; sulfide; water purification

1 Introduction

Water contaminations with heavy metals in galvanic and other industrial effluents may cause problems because highly expensive measures have to be performed to reach the set limits. Especially complexing agents keep heavy metals in solution even in the presence of sulfur containing precipitating agents. Organic sulfides like mercaptotriazines have been recommended as agents for heavy metal precipitation from those wastes [2]. In some cases, these sulfides may give better results. In other cases, they are less powerful than inorganic sulfides. Organic sulfides may have the disadvantage of high toxicity to the environment. Especially thiocarbamates may cause problems. These agents have to be used with great care to prevent overdosages. Resin sorbents and, recently, papers sorbents (gaiasafe paper) [3] have been recommended to overcome these problems. We developed gaiasafe-Formstoff as a new kind of activated, carbon-containing, inorganic sulfur agent to overcome the mentioned problems. We tested lead removal from wastewater with a heavy load of complexing agents (as an example, heavy metal). Further investigations with other heavy metals are under way. Here, we present the results of our lead tests. These results encourage us to recommend gaiasafe-Formstoff as a new kind of activated carbon agent for waste treatment.

2 Experimental

gaiasafe-Formstoff is a gray-black powder consisting of carbon and sulfides with a bulk density of 560 g/l. We tested the lead precipitation power of gaiasafe-Formstoff in comparison to different alternative solid and liquid agents and our gaiasafe paper. Atomic absorption spectrometry (AAS) has been used for lead detection. Lead detection limits where 0.05 mg/l.

2.1 Treatment of a high, lead-bearing wastewater with high complexant content

200 g waste sludge originating from an accumulator production plant was mixed with 1.8 l tap water. It is known, that the humic acid content in the waste prevents lead from precipitating. This was simulated by adding a sodium salt of humic acid to the mixture. The sodium salt of humic acid was delivered by Bakelite AG, D-34621 Frielendorf. The filtered mixture, the resulting dark brown *model waste water E*, contained 1000 mg/l of the sodium salt of humic acid, had a lead content of 240 mg/l and a pH of 9.9.

2.1.1 Treatment of model wastewater E₁ by solid reagents in a fixed filter bed

Model wastewater E has been diluted by tap water to get the necessary quantity. This dilution gave *model wastewater* E_i . Water E_i had a lead content of 110 mg/l, a pH of 9.9 and a dark-brown color. A fixed bed of 60 ml agent particles have been fixed between cotton wad within a glass pipe with a 5 cm diameter inside. This resulted in a Filter bed height of 5 cm. *Model water* E_i was passed from the bottom to top of the fixed bed filter at a transfer rate of 3.5 ml/min. After a throughput of 250 ml, the following quantity of 50 ml has been analyzed. Fixed beds were made from four different kinds of solid reactive particles:

gaiasafe-Formstoff	sulfide containing activated carbon, del. by gm-Ingenieurbüro, D-35274 Kirchhain		
Amberlite IRC 748	iminodiacetate functions containing styrene-divinylbenzene-copolymer, del. by Rohm and Haas Deutschland GmbH, D-60489, Frankfurt		
Purolite S 930	iminodiacetate functions containing styrene-polymer, del. by KSN Wassertechnik, D-57647 Niestetal		
gaiasafe paper E	impregnated paper on the base of active metal oxide sorbents, cut into pieces of 1 x 1 cm, del. by gm-Ingenieurbüro, D-35274 Kirchhain		

21.2 Treatment of model wastewater E by liquid reagents

 $250 \ \mu$ l liquid lead precipitation reagent was mixed with 100 ml *model wastewater E.* After a reaction period of 20 min, the reaction mixtures have been filtered. Different liquids were used as lead precipitation reagents:

Metalclean B	monothiocarbonate solution, delivered by Oecoproducts International S.P.R.L	
Nalco 71281	dithiocarbamate solution, delivered by Deutsche Nalco-Chemie GmbH, D-60486 Frankfurt/Main	
TMT 15	trimercapto-s-triazine-trisodium-salt solution, delivered by Degussa AG, D-63403 Hanau	

Table 1: Results of 2.1.1 and E (240 mg/l lead 2.1.2)

3 Results, Discussion and Recommendations

Test results of water treatment tests 2.1.1 and 2.1.2 with high lead-loaded waters and high complexing agent concentrations are collected in **Table 1**. Test results of water treatment test 2.2 with low lead-load levels are collected in **Table 2**.

gaiasafe-Formstoff demonstrated the best results of the lead reduction tests as well as a fixed-bed reagent or, by adding it as a solid, particles with all kinds of test waters even in waste waters containing high levels of complexing agents.

These results encourage us to recommend gaiasafe-Formstoff powder as wastewater treatment agent for heavy metal reduction by fixed filter bed. This product has clear advantages over known metal reduction reagents. After use it has the benefit of possible metallurgical recycling of its heavy metal sulfide load and elemental carbon load as an ore and coke substitute in metallurgical processes. The heavy metal content in the dried reaction product of gaiasafe-Formstoff may be enriched to more than 1 kg of heavy metal per kg of gaiasafe-Formstoff. Flocculated by means of iron salt or by means of organic flocculents in gravel bed filters, and gathered from the filter backwash as a filter press cake gaiasafe-Formstoff represents from metallurgical view a mixture of pure ore and elemental carbon representing an energy rich ore component. As a valuable substitute ore used, Formstoff may represent an effective example step of metallurgic, raw-material recycling.

We started investigations with gaiasafe-Formstoff about its ability to reduce the contents of further heavy metals in waste

test	water treatment agent	lead content after fixed bed treatment, mg/l	lead reduction ratel, %	color of treated water
1.1	gaiasafe Formstoff	2.8	98	yellowish
fixed bed	Amberlite IRC 748	11.2	90	dark brown
	Purolite S 930	19.2	83	dark brown
	gaiasafe paper E	64	42	dark brown
1.2	Metalclean B	169	30	dark brown
liquid	Nalco 71281	14.7	94	dark brown
treatment	TMT 15	163	32	dark brown

Table 2: Results of water treatment test 2.2 with model water F containing low lead concentration (3.05 mg/l lead)

water treatment agent	lead content after fixed bed treatment, mg/l	lead reduction rate, %
gaiasafe-Formstoff	< 0.05	> 98
Amberlite IRC 748	1.99	34
Purolite S 930	1.00	67
gaiasafe paper E	0.094	97
Metalclean B	1.41	54
Nalco 71281	0.074	98
TMT 15	0.145	95

2.2 Treatment of wastewater F by solid and liquid reagents

Wastewater F, originating from an accumulator production plant, with a pH of 7, had a lead content of 3.05 mg/l. 100 mg of solid reagent or 100 μ l of liquid reagent was mixed with 500 ml *wastewater F.* After a reaction time of 24 h, the reaction mixtures have been filtered. As lead sorbing reagents most solids and liquids described in 2.1.1 and 2.1.2 were used:

gaiasafe Formstoff, Amberlite IRC 748, Purolite S 930, gaiasafe paper E, Metalclean B, Nalco 71281, TMT 15.

waters. We see special advantages for the decontamination of different kinds of waste like galvanic effluents, acid mine drainages and flue gas cleaning effluents.

We recommend the use of gaiasafe-Formstoff in wastewater treatment processes in the form of powder which is mixed to the wastewater in weak over-dosage concerning to heavy metal content. In relation to wastewater conditions, as much as 1 kg of lead may be precipitated and sorbed by 1 kg of gaiasafe-Formstoff or less. The necessary minor surplus of gaiasafe-Formstoff in relation to lead will cause small sulfide contents in the resulting effluents. This sulfide content may be eliminated easily by well-known means.

4 References

- TALBIERSKY, J., GLASER, H., OESTE, F.D. (1995): Formstoffe und deren Verwendung. Deutsche Offenlegungsschrift der Patentanmeldung vom 31.12.1994, Az.: P 44 47 317.6
- [2] PELDSZUS, R. (1995): TMT 15 / Natriumsulfid zur Quecksilberabscheidung. Vortrag zum VDI-Seminar "Additive in Verbrennungs- und Feuerungsanlagen" 13.-14. 2. 1995, Düsseldorf
- [3] HAAS, R., OESTE, F.D. (1999): Imprägnierte Filterpapiere für die Wasserreinigung. UWSF – Z. Umweltchem. Ökotox. 11, 20

Received: March 15th, 1999 Accepted: June 21st, 1999