Impact of bentonite treatment on the heavy metal content in fruit juices

| Bentonite | Heavy Metal | Fruit Juice Treatment | Solubility |

Introduction

Fruit juices are not only appreciated and enjoyed for their delicous taste, they are also considered to contribute significantly to a healthy and sustainable nutrition. Consequently quality demands regarding the content of undesirable contaminants (heavy metals among others) in the semi-finished and finished products offered are high. The fruit juice industry has accepted responsibilty and has long since defined maximum values for the respective heavy metals in the generally accepted Code of Practice. These standards are subject to constant revision. For instance, the significant reduction of the accepted lead content from 50 µg/L to 30 µg/L is about to come. The intensified activities of food control and consumer protection organisations in connection with the further development of analytical methods lead to an increased sensitization of the food trade and the consumers. Caused by the quality standards of the trade for finished products, specifications of semi-finished fruit juice products individually agreed upon, could thus possibly be more stringent than those of the industry in general. In this connection, the fact that heavy metals are part of our environment and that therefore not even natural raw materials are free from heavy metals is often overlooked. Furthermore subsequent process steps still contribute to increase concentrations. In this respect the mineral adsorbent bentonite must be critically examined. For the production of clear and particularly stable fruit juices and juice drinks the use of bentonites which are suitable for foods is a must. The available enzymatic and physical methods do not sufficiently stabilise semi-finished fruit juice products to obtain complex blends. Being a clay mineral, bentonite potentially contains all elements of the periodic system yet in very different amounts. The evaluation of PuroBent®, a particularly low-in-heavy metal bentonite, shall be described with the present study.

Tab. 1: Recommendations of the AIJN Code of Practice

Iron (Fe):	max. 5.0 mg/L	Arsenic (As):	max. 100 µg/L
Copper (Cu):	max. 5.0 mg/L	Lead (Pb):	max. 50 µg/L
Zinc (Zn):	max. 5.0 mg/L	Mercury (Hg):	max. 10 µg/L
Tin (Sn):	max. 1.0 mg/L	Cadmium (Cd):	max. 50 µg/L

How do heavy metals enter into the fruit juice?

Heavy metals are a natural ingredient of vegetable metabolic systems and beyond that are further cumulated directly from the biosphere of fruit processing and possibly by subsequent processing steps. The impact of the treatment of fruit juices during processing was, for the first time, examined more comprehensively in a work by *Dietrich* and *Nissen 1998*[1]. The authors determined the respective intake caused by the processing steps and the use of technical aids in practical processing trials. Tests at a black currant juice as example (see fig. 1) showed that above all the bentonite treatment (increase by 40 %) and the precoat filtration with kieselguhr (content more than doubled) lead to increased arsenic contents, reason enough to critically check soluble bentonite ingredients.

Elements in bentonite and their solubility:

As a mineral obtained by mining, bentonite more or less contains all elements of the periodic system, even though concentrations vary strongly. A migration of these elements

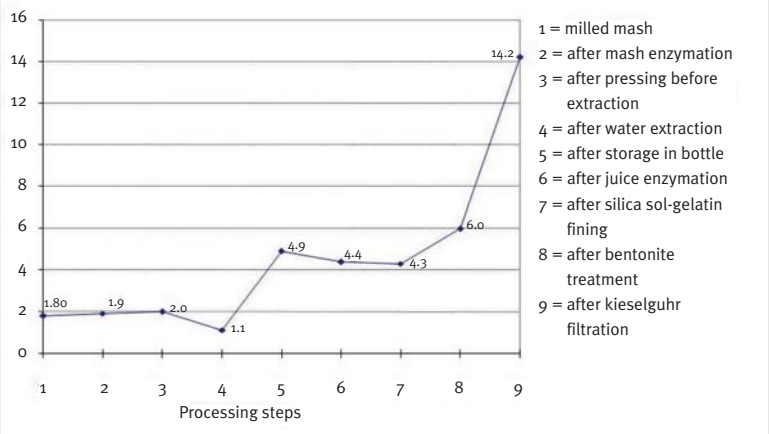

Fig. 1: Changed arsenic concentrations (µg/L) in the course of processing (Dietrich and Nissen, 1998)

Tab. 2: elements in bentonite and their solubility

Element	Al (mg/g)	Fe (mg/g)	As (µg/g)	Pb (µg/g)
Total content in bentonite (average values)	105	59	5	30
Release in tartaric acid extract according to OIV method	0.7 - 1.2	0.3 - 2.0	0.4 - 2.0	1.0 - 7.8
Increase of content in the juice by bentonite according to study 1998[1]	0.52	0.35	1.7	11
Soluble portions related to total content (%)	0.7 - 1.1	0.5 - 3.4	8 - 40	3 - 26

into the medium e. g. during fruit juice fining, strongly depends on how stable their bonding to the crystal lattice is (see tab. 2). Silicium and aluminium, the elements which are present in the largest amounts, have a rather poor solubility. Also iron with an average total content of approx. 6 % is very poorly soluble. The measurement of the soluble portions is performed according to OIV (Resolution OENO 11-2003) in a 1 % tartaric acid. Compared with the results of *Dietrich* and *Nissen 1998*[1] in tab. 2, this method provides a roughly realistic evaluation of the intake in the course of acidic beverage fining. It can be clearly seen that the heavy metals, particularly arsenic and lead, despite low total contents dissolve in relatively large proportions. Obviously these elements – at this stage present as ions – fit badly into the bentonite crystal lattice with their size and charge.

When the arsenic and lead releases of conventional commercial bentonites applied for beverage treatment are closely examined, the broad range of measured values becomes clear (see fig. 2). Soluble arsenic concentrations are between 0.3 and 4.0 µg/g, lead contents range between 2 and 15 µg/g. With normally applied additions of 200 g/100 L, concentrations in the juice increase with extreme cases by up to 8 µg/L(arsenic) or by up to 30 µg/L (lead), when higher amounts are used for treatment, concentrations are accordingly higher (see tab. 3).

Table 3 clearly describes that in view of the broad variation range, bentonites with low heavy metal release lead to relatively low contents in the juice even when added in high

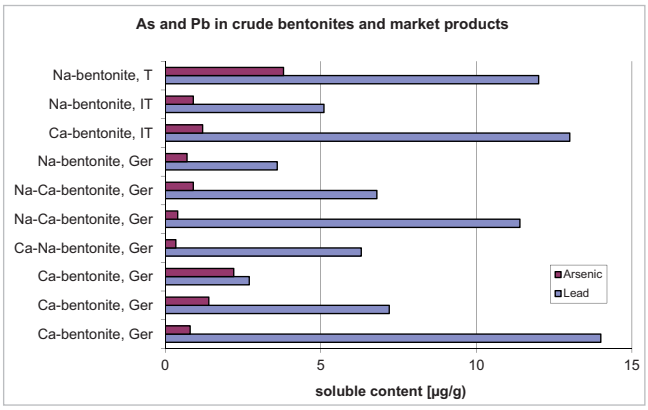

Fig. 2: Arsenic and lead concentrations (according to OIV-method) in conventional bentonites

Tab. 3: Increase of contents in the juice when bentonites with low and high iron and heavy metal contents are applied

Element	Content in bentonite (soluble)	Increase of content in the juice with fining conducted with			
		100 g/100 L	200 g/100 L	400 g/100 L	800 g/100 L
Arsenic	0.3 µg/g	0.3 µg/L	0.6 µg/L	1.2 µg/L	2.4 µg/L
	4.0 µg/g	4 µg/L	8 µg/L	16 µg/L	32 µg/L
Lead	2 µg/g	2 µg/L	4 µg/L	8 µg/L	16 µg/L
	15 µg/g	15 µg/L	30 µg/L	60 µg/L	120 µg/L
Iron	0.3 mg/g	0.3 mg/L	0.6 mg/L	1.2 mg/L	2.4 mg/L
	2.0 mg/g	2 mg/L	4 mg/L	8 mg/L	16 mg/L

amounts. With other bentonites however, this is already the case with the usually applied amounts.

PuroBent® – a new, low-in-heavy metals bentonite for the treatment of beverages

Bentonite is a natural clay mineral and thus, can only to a limited extent undergo purification processes without affecting its application properties. Therefore the provision of a bentonite of assured low heavy metal content requires careful selection of the raw materials used and a constant and consistent control of critical parameters. The aim of PuroBent® development was a soluble As-concentration of significantly below 1 µg/g, a Pb-concentration of maximally 4 µg/g (in tartaric acid extract) and a release of iron of maximally 0.5 mg/g.

These values laid down for the raw materials used for PuroBent® production undergo permanent monitoring. Otherwise this bentonite is a sodium-calcium bentonite of moderate Na-content (‹ 1 % release) and standard application characteristics.

Application trials in fruit juice production

In application trials with model solutions and fruit juices tests were conducted to determine in how far the low heavy metal releases affect practical operation. PuroBent® was analysed in comparison with conventional commercial bentonites. Very deliberately a spectrum ranging between usual application and extreme overdosing was chosen when performing the trials. Then, once again, it was clearly shown that a bentonite application even with higher amounts added will hardly exceed the limiting values of the Code of Practice in fruit juices. In single cases however, the by far more stringent guide values for drinking water or even mineral water for the treatment of baby food can be used for assessment. In these cases, normal additions of standard bentonites may result in the exceeding of a critical level. Merely when PuroBent® was applied, concentrations remained below 5 µg/L, also with the extreme dosage of 12 g/L, whereas, dependent on quality (see fig. 2), other conventional bentonites after addition of these amounts, showed concentrations of more than 15, respectively 20 µg/L. Thus significant differences in relevant heavy

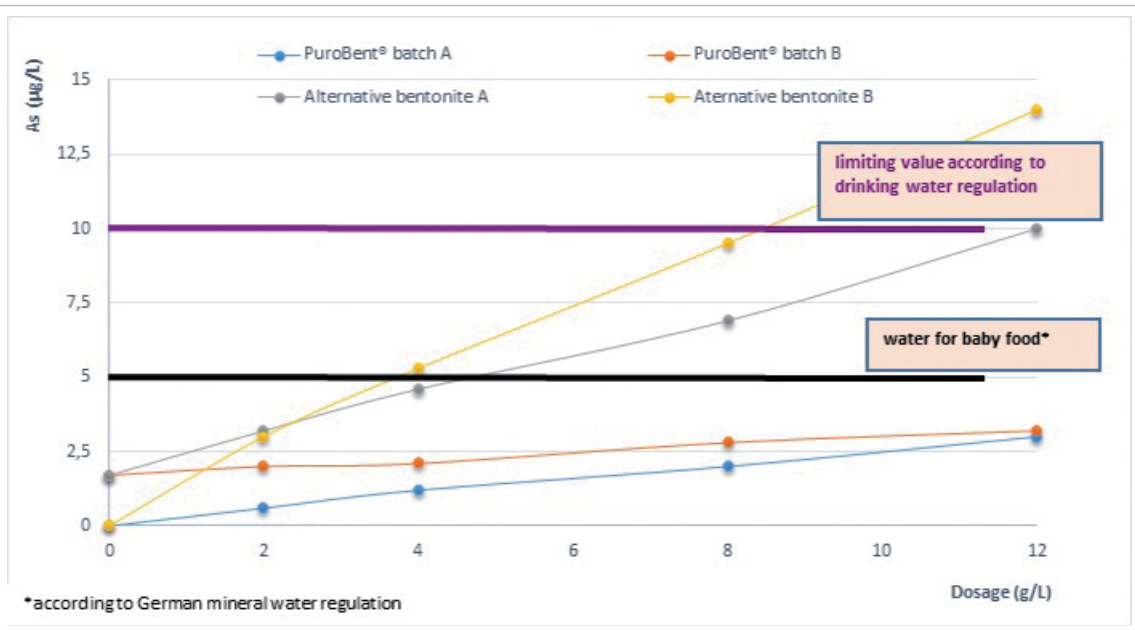

Fig. 3: Treatment of two apple juices with two batches of PuroBent® and two alternative bentonites, increase of arsenic content dependent on added amount

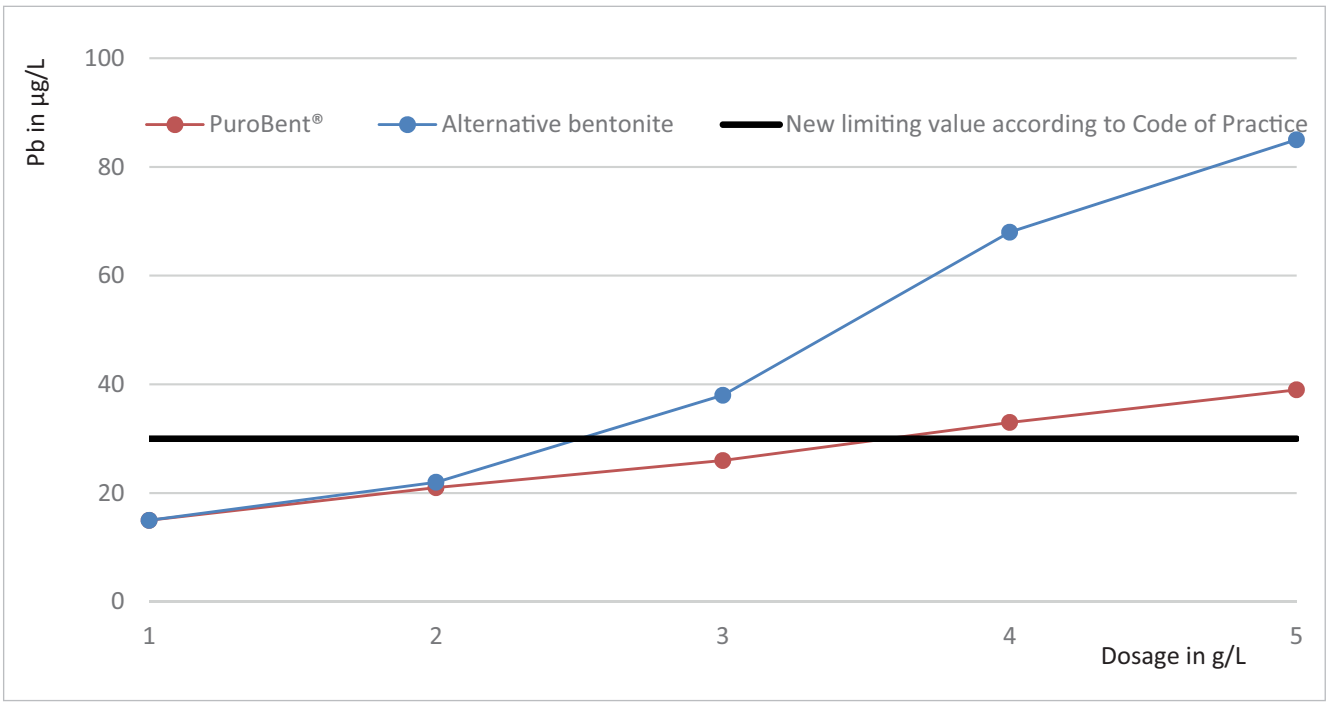

Fig. 4: Treatment of an apple juice with PuroBent® and with an alternative bentonite, increase of lead content in dependence of addition

metal concentrations result during PuroBent® application in comparison with standard bentonites, even though concentrations are far from being legally relevant or in any way hazardous to health.

With regard to lead the tendency for higher concentrations during juice treatment is still more distinct. As shown in figure 4, the initial juice already contained remarkably high concentrations. While when PuroBent® is used, the increase remains moderate, lead concentrations with the alternative bentonite quickly rise to more than 30 µg/l when more than 2 g/l are used. In view of reduced limiting values in the Code of Practice a bentonite with low heavy metal content should be generally used if raw materials have a high heavy metal load in advance.

Conclusion

The requirement to produce fruit juices with heavy metal concentrations as low as possible will still grow in the future with the increased activities of consumer protection organisations. The treatment of fruit juices with bentonite is indeed only one source of heavy metal intake within the manufacturing process and has less effect compared to kieselguhr filtration, nevertheless should be closely watched over. Bentonites contain very different contents of soluble heavy metals, important for their amounts are, above all, arsenic and lead. With the usual moderate additions of 100 – 200 g/100 L concentrations in the juice also remain at a relatively low level (dependent on the initial content). For the production of fruit juices which must meet stringent specification requirements, the low-in-heavy metals special bentonite PuroBent® is the suitable treatment agent. If additions of more than 500 g/100 L are required, PuroBent® should absolutely be used, since also with extreme additions problematic heavy metal concentrations are not to be expected. By permanent monitoring of the raw materials a constantly low heavy metal content of this bentonite product is assured. Since also kieselguhr (diatomaceous earth) plays a part in this connection, suitable mixtures of kieselguhr-free filter aids as alternative to a targeted poor-in-heavy metals overall treatment concept are available.

Literature

1 Dietrich, H.; Nissen, C. Herkunftsquellen für Blei im Wein sowie Schwermetalle in Fruchtsäften und Möglichkeiten zur Vermeidung bzw. Verminderung von Kontaminationen. Geisenheimer Berichte Bd. 36. 1998

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