Degradation of Organic Substance in Sewage with Functional Materials Made from Rare Earth Residue and Examination of Its Genetic Toxic on Aquatic Organism

Ying Zhang [1], Shiying Liu [1], Nanqi Wen [2]

(1. School of Resource & Environment, Northeast Agricultural University,
Harbin, Heilongjiang 150030, China;
(2. School of Municipal & Environment Engineering, Harbin Institute of Technology,
Harbin, Heilongjiang 150090, China, liushiy@mail.china.com)

Abstract: This study used low radioactive rare-earth waste as raw materials, which were made into special functional materials. The radioactivity of these special functional materials complies with the healthy protect standard of radioactive materials (GB6566-86). The tests showed that the special cement could lower COD, the degradation rate increase when the time was prolonged. In acidic medium, they could remove E. Coli effectively. Applying aeration and adding lumps of cement, data indicated that aeration adding lumps of cement had synergistic action on sewage treatment. Moreover, the micronuclei and abnormal nuclei rates of peacock fish were tested, genetic toxic effects of rare-earth waste and its special functional materials (cement, plastic) on peacock in water were investigated. Results show that the leachate of rare-earth waste could lead to micronuclei and abnormal nuclei rates of peacock fish an obvious increase ($P<0.01$). Products made from the waste caused the micronuclei rate to be increased because of its low radioactive action, but the change in abnormal nuclei rate could not reach a remarkable level. It showed that rare-earth waste had a certain effect of causing mutation on aquatic organism. Harmfulness of products made from this waste was decreased largely, and resources could be effectively saved. [Nature and Science, 2004,2(2):15-19]

Key words: functional materials made from rare earth residue; the degradation rate of COD； number of coliform group bacteria; peacock fish; micronuclei-rate; abnormal nuclei rate.

1 Introduction

China is rich in rare-earth, reserves of it occupy 80% of that of the whole world, as resources of rare-earth waste is becoming serious social problem day by day (Ding, 1995; Hu, 1996; Wang, 1991). As to rare-earth material factories in Harbin (these factories are small and medial scales), nearly 1000 ton waste is stored up and because of its piling up, the nearby hilly area is become deharvested. Health of human and livestock is greatly harmed. Components of the waste contain radioactive nuclide ^{232}Th, and the specific activity of the waste is 5000-8000 Bq/kg, it is 20 times diluted and used to make special cement and plastic pipe, their radioactive dosages chime in with the standard for limitation of radioactive matters contained in industrial wastes used as building materials (GB6763-86), therefore, it provides an effective way to use low radioactive rare-earth waste (Lin, 1993).

We find that this special cement can lower COD and remove E. Coli after being dipped in sewage. Thereby we have used this kind of product for experiments and done some researches in detail. We intend to use these special cement and plastic to make drainage pipes. In order to know the genetic toxic effect of radiation, and use the low radioactive waste safely and reasonably, in this study, the chromosomal aberration of circumambient erythrocytes has been observed, and the appearance rates of micronucleus, nucleus protrusion, nucleus endo-hollow, enod-vacuole and double-nuclei are used for judgment (these are called abnormal nuclei rates) (Meng, 1999; Wang, 2002; Zhang, 1984).

2 Degradation Test of Organic Substance

2.1 Materials and methods

Cement test piece: (Specification 50x40x40 mm^3). Adding a controlled amount of low radioactive rare-earth waste in cement to meet the National standard, then, the cement was rectangular, and provided by cement branch of Mao-er mountain steelworks, Shang-Zhi city, Heilongjiang province. To make skin state stabilization, all of lumps of cement had been dipped into distilled water for 72 hr and changed water once 24 hr.

$K_2Cr_2O_7$ method was adopted in test of COD. The experiments were divided into 2 groups:（1）took 1000 mL Majiagou sewage apiece; added 3, 6, 9 lumps of cement separately; treat 2, 4, 6 hr; measure COD and calculated degradation rate.（2）took 500 mL Songhuajiang brewhouse sewage apiece; put into two beakers; applied aeration and aeration adding 6 lumps of cement to sewage treatment; after 4、8、24、28、48 hr，measure COD.

Fermentation method was adopted in test of number of coliform group bacteria. Glass electrode method is adopted in test of pH. Concentrated sulfuric acid was analytical pure (each drip about 0.05 mL). The experiments were divided into 4 groups: took 100 mL Majiagou sewage apiece,（1）primary sewage was control;（2）sewage added one lump of cement;（3）sewage added 1 d H_2SO_4;（4）sewage added one lump of cement and 1 d H_2SO_4. After 4 hr, measure pH and number of coliform group bacteria separately.

2.2 Results and analysis

The results indicate that we can get the higher rate of degradation by adding more lumps of cement under the same sewage volume (Figure1). Prolonged the treatment time, COD shows a descending trend.

The tests suggested that this kind of low radioactive cement could lower COD.

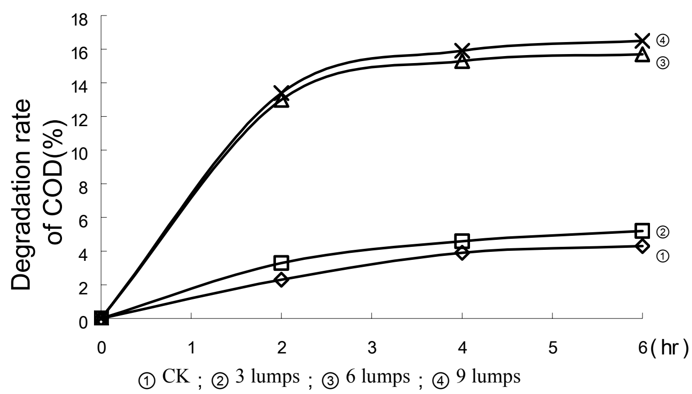

Figure 1 Effects of lumps of cement on degradation rate of COD in sewage (%)

The effects of lumps of cement on COD in sewage under aeration condition are showed in Table 1. The sewage is treated by simple aeration condition and aeration adding lumps of cement condition separately. It shows that aeration adding lumps of cement can save treatment time and get better effect. It indicates that aeration and adding lumps of cement have synergistic action on sewage treatment.

Measurement of number of coliform group bacteria is showed in Table 2. The action that low radioactivity rare-earth waste product (lumps of cement) has on E. Coli is evaluated by number of coliform group bacteria (No./L). In acidic sewage, this special cement can remove E. Coli effectively

Table 1 Effects of lumps of cement on COD in sewage under aeration condition (mg/L)

Treatment	0h	4h	8h	24h	28h	48h
Simple aeration condition COD (mg/L)	1321.72	1059.83	957.53	626.03	568.79	181.15
Aeration add lumps of cement COD (mg/L)	1321.72	937.90	867.50	474.67	396.92	91.39

Table 2 Effects of lumps of cement on coliform group bacteria under different pH of sewage (No./L)

Treatment	pH	No. of coliform group bacteria after 4h
1 Primary sewage	6.98	2.3×10^5
2 Sewage + one lump of cement	6.98	2.3×10^5
3 Sewage + 1d H_2SO_4	6.5	4.4×10^2
4 Sewage + one lump of cement + 1d H_2SO_4	6.5	<9

3 Examination of genetic toxic

3.1 Animals used for experiment and feed

Pea-cock fish (Kubi fish or rainbow fish is called) it belongs killifish order, bright-colored killifish family, tropical small decorative fish, the suitable water pH value is in the range of 7.2-7.4, length of its body is 2.5-5.0 cm, weight about 2.2 g, bought from the flower-bird-fish market, After one week long domestication in the lab, healthy and active ones are selected to be tested. Feed is chose from the market and kept fresh.

3.2 Source of experimental medicines, rare-earth waste and its products

(Cyclo phosphamide cp): produced by the 12th pharmaceutic factory; Giemsa mother liquor; 1 g Giemsa is dissolved in 66 mL glycerine at 56°C, then, 66mL methyl is added to form the mother liquor and is kept in brown bottle.

Rare-earth waste: it contains a micro-amount of ^{232}Th, $CaSO_4$, $BaSO_4$ occupy more than 90% and provided by Harbin refractory material factory.

Cement test piece: see 2.1

Plastic Pipe: provided by the 2nd plastic factory, Qi-Tai-He (Mixed with rare-earth waste and tube-shaped moulded thermo-plastically): Φ100mm, meet the National standard.

(Note: cement piece, plastic pipe are made from diluted rare-earth waste which has the specific activity of 5000-8000 Bq/kg, and it is met GB6768-86 standard.

3.3 Test methods and photographic technology

Put rare-earth waste, plastic tube, cement piece into 2000mL fish-feeding tanks respectively, where the cement piece and plastic tube are pre-soaked for 3 days (72 hours), the soaked water is changed each day. The two products have the contact area of some 1000 cm^2 with water.

Raising pea-cock fishes in 3 tanks mentioned above for 12 days respectively, removing sludge settled in tanks and adding fresh water periodically. Feeding with fresh and active food each day, one negative contrastive group is prepared. 10 fishes are used for each group, after 12 day feeding, cut down fish tails and have fish blood sampling, make films in routine smear way, fixed by methyl alcohol, naturally dried for 1 min, dilute Giemsa mother liquor by buffer of phosphoric acid with the ratio of 9:1 and take it as working liquid, 1 smear for each fish, selecting the area that is smeared evenly, has a moderate density and is well dyed to be microscopic-examination one, then, change the eyepiece and use a suitable one to observe, noting down numbers of micronuclei, nucleus protrusion, nucleus endo-hollow, endo-vacuole and double-nuclei, then, the fractional percents of micro-nuclei and abnormal nuclei are calculated and treated statistically by percent "t" examination.

The PM-10ADS photographic system of Japanese OLYMPUS optical microscope is used to take photos of the ideal chromosome specimen observed by optical microscope, under the condition of oil-submerged objective lens 100XNFK 3.3 (and NFK5) times, using GB21° black-white film to take photos, and amplified with No. 3 photo-paper.

3.4 Experimental results

The experimental results are shown in table 3, statistic analyses show that rare-earth waste in water can cause obvious increase in micro-nuclei rate and abnormal nuclei rate of pea-cock fish, its products plastic and cement test groups have the mutagenic effect much lower than that of the rare-earth group, and the difference is very remarkable (P<0.01). The reason is that ordinarily, ^{232}Th radiates 3 kinds of ray, α - β - γ ; they occupy the ratio of radiative energy as follows α ~81%; β :15%~16%; γ :2~3% . The order of ability is $\alpha > \beta > \gamma$. When reacts with water, the ability of α particles is tens of million times higher than that of reacting with gas, this is main reason of its toxic effect on aquatic organism. As to products of rare-earth waste-plastic group and cement group, because of their low radiative actions making the micro-nucleus rate increase compared with negative contrast group. The abnormal nucleus rate has the tendency to increase, but it is not remarkable, this shows that the use of rare-earth waste products is relatively safe.

Table 3 Genetic toxicity effect of rare-earth waste and products of rare-earth waste on peacock fish

Group	No. of cells observed	Nucleus protrusion	Nucleus endo-hollow	Nucleus endo-vacuole	Double -nuclei	Micro-nucleus
1 Control	10120	30	34	1	4	1
2 Rare-earth waste	12186	131	308	12	32	18
3 Plastics	10321	31	94	1	4	5
4 Cement	10135	47	96	5	18	8

Group	Cell No. With abnormal nuclei	Micronucleus Rate(‰)	Rate of abnormal nuclei(‰)	P
1 Control	70	0.10	6.92	-
2 Rare-earth waste	501	1.48	41.11	P<0.01
3 Plastics	135	0.48	13.08	P>0.05
4 Cement	174	0.79	17.16	P>0.05

4 Conclusion and Discussion

(1) Mixing radioactive rare-earth waste in industrial raw materials, and using it safely, reasonably, it is one of the effective ways to reuse rare-earth waste and save the natural resource.

(2) The special cement which containing low radioactivity rare-earth waste can lower COD, the degradation rate increase as the time go on. In acidic sewage, this special cement can remove E. Coli effectively. Aeration and adding lumps of cement which containing low radioactivity rare-earth waste has synergistic action on sewage treatment.

(3) This study shows again that induced mutagen is related to dosage, the higher dosage of rare-earth waste, the higher mutation. Its products, micro-nucleus rate and abnormal nucleus rate of cement group is higher than that of plastic group, this is considered that is because of natural radiativity of cement. This study is made in winter (time), the water temperature indoor is (as low as) at 16° C, it shows that the experimental material used in the study –peacock fish may be used as a monitor-organism for showing the mutagenic pollutants in fresh water in the north.

(4) As to genetic toxic effect of products made from rare-earth waste, a basic study is done only. Because the range of α ray is only a few cm, may be shielded completely, so, it is still inferable that rare-earth waste products used as sewerage pipe is safe to a certain extent. For safety, it needs deeper research to prove.

Acknowledgement

This project is supported by Harbin city subject leader fund (9971218026).

References

[1] Ding W. Survey of rare earth in China soil [J].Rare Earth , 1995 , 6: 44-8.
[2] Hu Q. Aquatic ecological environmental effect of rare earth elements [J]. Environmental Pollution and Control , 1996 , 3:28-30.
[3] Lin H. Disposal of waste in rare earth production [J]. Rare Earth , 1993;14(1):34-6.
[4] Meng ZQ, Zhang B. Polymerase chain reaction-based deletion screening of bisulfite (sufur dioxide) - enhanced gpt-mutants in CHO-AS52 cells [J]. Mutat Res , 1999, 425:81-5.
[5] Wang L. Micro-nucleus test of chlorine dioxide and chlorate in water [J]. Journal of Harbin University of Civil Engineering and Architechture , 2002 , 35(1):58-60.
[6] Wang Y. Content and distribution of rare earth elements in soil [J]. Environmental Science, 1991 , 5:51-4.
[7] Zhang GJ. Mutation Cancer and malformation [M]. New York. 1984 , 25-36.