A SUITABLE INTEGRATED TECHNOLOGY FOR THE COMPLETE TREATMENT OF ORANGE/DIOXIN IN SOILS AND SEDIMENTS IN VIETNAM

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Introduction

Currently at Bien Hoa airport there is huge volume (estimated about 350,000m^3) of orange/dioxin contaminated soils and sediments with complex composition, high concentration and unequal and random distribution of pollutants. Therefore, there are difficulties in applying proven methods in the world in Vietnam.

It is urgent to develop a suitable method for the complete treatment of orange/dioxin in soils and sediments in Vietnam. In the project KHCN-33.02, Chemical division of People's army of Vietnam has studied and developed the a suitable integrated technology (washing by the surfactant solution, combined with chemical and physiochemical treatment, then, oxidation by catalysts at low temperature) for the complete treatment of orange/dioxin in soils and sediments in Vietnam. The results from the study of the integrated technology for the complete treatment of orange/dioxin in soils and sediments at Bien Hoa airport will be reported in this paper.

Materials and methods

Materials and chemical

Activated carbon (AC_4 - Japan) as particle type; Surfactant S2 with critical micelle concentration (CMC) of 61 ppm at 25 ^{0}C; The solution of nano $Fe^{(0)}$ and catalyst nano CaO/Fe_3O_4 manufactured in Vietnam.

Determination of concentration of Orange/Dioxin in the soil and in the surfactant solution.

Concentration of 2,4-D, 2,4,5-T is calculated based on the EPA analysis method 8151A; Concentration of dioxin is calculated by the EPA method 8280B.

Treatment efficiency

$$H\% = \frac{C_0 - C}{C_0} \times 100\%$$

Where:

C_o : Concentration of pollutants in the soil before treatment.

C : Concentration of pollutants in the soil after treatment.

Pilot line of integrated treatment technology for Orange/Dioxin in soils and sediments.

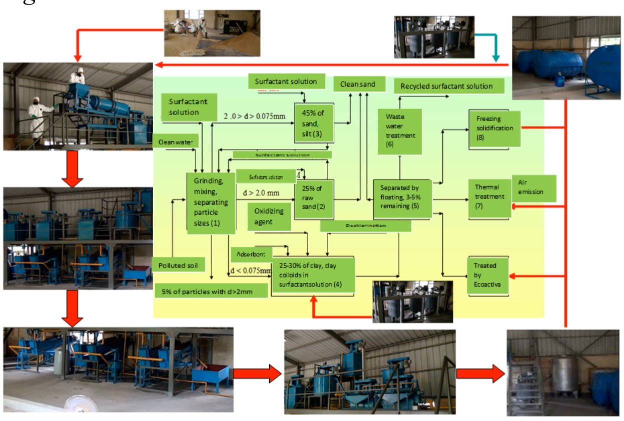


Fig 1: Process flow of the integrated technology

Results and discussion

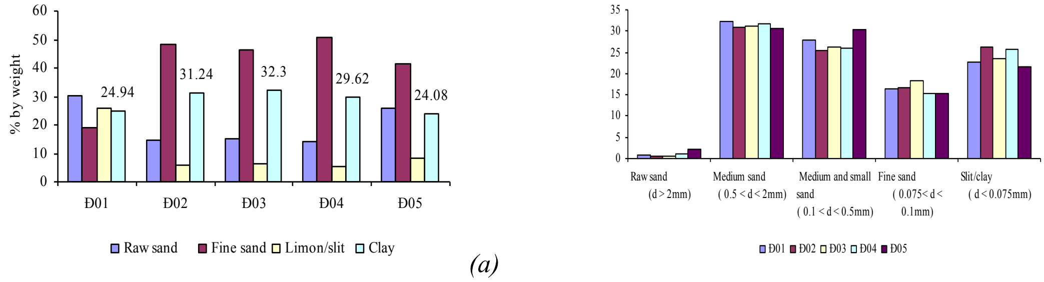
Pedological composition of the contaminated soil at Bien Hoa airport.

Pedological investigations at Bien Hoa airport show that mainly rocks, ground and sands at the depth of 0-0.6 meters, stiff brown mixed clays in at depth of 0.6-1.3 meters, mixed clays, mixed clay of spotted pale pink and pale yellow in plastic stiffness to medium stiffness at the depth of 1.3-4.6 meters and mixed clays in different colours of cement gray, pale yellow, blue gray and brown at the depth of 4.5-10.2 meters. Results of agrochemical analysis of soil samples are displayed in the table 1.

Table 1: Results of agrochemical analysis of soil samples

No	Name of sample	Agrochemical analysis of soil samples										
		OM (%)	Ds (kg/dm3)	HU (%)	CEC (Clay)	Raw sand (%)	Fine sand (%)	Slit (%)	Clay (%)	ΣAl(%)	ΣFe(%)	As(ppm)
1	Đ01	0.61	2.49	0.008	12.78	30.12	19.14	25.8	24.94	3.08	2.16	22.7
2	Đ02	0.27	2.45	0.004	16.78	14.83	48.21	5.72	31.24	2.72	0.74	727.5
3	Đ03	0.34	2.57	0.008	17.96	15.36	46.26	6.1	32.3	2.65	0.84	26.5
4	Đ04	0.61	2.49	0.008	13.32	14.23	50.89	5.26	29.62	2.54	0.93	48.2
5	Đ05	0.68	2.66	0.008	14.62	25.91	41.69	8.32	24.08	2.82	1.18	46.2

Đ01; Đ02; Đ03; Đ04 and Đ05:Soil samples in the PACE IVY area



(a) *(b)*

Fig 2: Pedological composition *(a)* and the distribution of particle size *(b)* in investigated soil samples at Bien Hoa airport, Dong Nai province.

Contamination levels of Orange/Dioxin in the soil at Bien Hoa airport.

By GC/MS technique, analysis results of pollutants are displayed in the tab 2:

Tab 2: Analysis results of main pollutants in soil samples at Bien Hoa airport

STT	Sample	Composition of contaminants				
		2,4D (ppm)	2,4,5T (ppm)	2,4 DCP (ppm)	2,4,5 TCP (ppm)	2,3,7,8 TCDD (ppt TEQ)
1	Đ01	10.76	16.15	0.37	0.79	4,624.39
2	Đ02	41.82	92.73	0.43	18.50	3,407.74
3	Đ03	17.21	23.37	1.29	0.94	10,858.78
4	Đ04	87.98	148.37	0.14	11.85	19,468.46
5	Đ05	69.56	117.24	1.53	5.62	22,242.69

Investigations show that there is huge volume of Orange/Dioxin contaminated soils and sediments with complex composition, high concentration and unequal and random distribution of pollutants. Therefore, it is difficult to achieve the effectiveness if only a proven single method is applied.

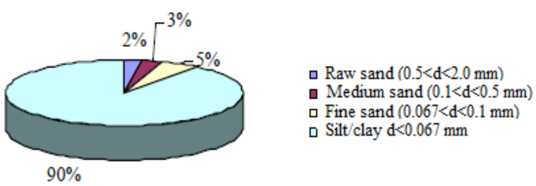


Fig 3: The distribution of 2,3,7,8 TCDD in the pedological composition of the sample Đ05

It is easy for Dioxin to combine irreversibly with organic compounds in the soil, especially humic acid, which is the main humus component of silt and clay. To evaluate the distribution of pollutants in the pedological composition of the soil, the research team has classified soil samples based on the particle sizes. The distribution of 2,3,7,8-TCDD in the pedological composition of the sample Đ05 is shown on the Fig 3.

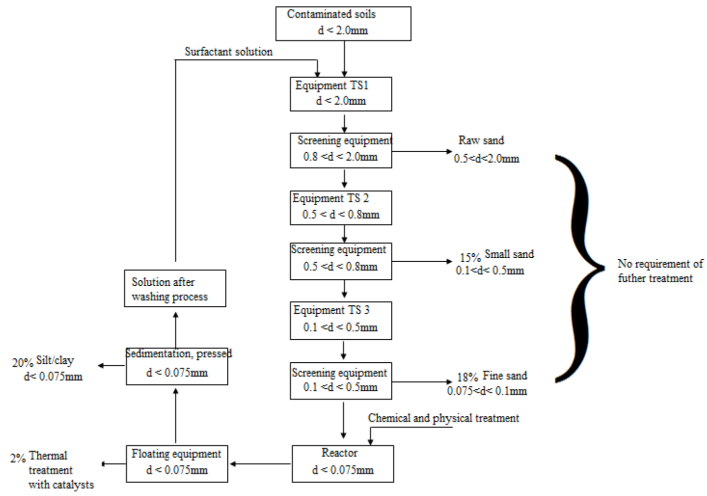
It is indispensable to the washing technology by surfactant solution as 90% of orange/dioxin is distributed in silt and clay which accounts for only 25% of the volume of the original soil.

A suitable integrated technology for the complete treatment of Orange/Dioxin in soils in Vietnam.

To treat Orange/Dioxin completely, there are many technologies, which have been studied, tested and applied. Depending on the advanced level of the method, characteristics of contaminated sources, volume of contaminated soils, environment criteria of each country and the budget, the suitable method will be selected.

In Vietnam, the criteria for selecting a treatment technology includes short-termed effectiveness and long-termed effectiveness to reduce the volume of pollutants, their toxicity and low cost. The accepted limit of Dioxin in soils and sediments in Vietnam is based on the standard of Vietnam: QCVN 45:2012/BTNMT.

Fig 4: Process flow of the integrated technology



As Orange/Dioxin are distributed mostly in silt and clay, then in the integrated technology, contaminated soils are washed by surfactants and screened by particle size to remove over 70% of the volume as sand, which has inconsiderable concentration of Orange/Dioxin and does not need further treatment. Orange/Dioxin in the solution and in silt/clay are further treated by chemical agents to decompose Orange/Dioxin in the smaller volume with higher reaction efficiency. Adsorbents are separated by floating process, with high concentration of Orange/Dioxin is thermally treated with the presence of catalysts. The soil washing solution is cleaned, added more surfactants and recycled.

Results of experiments in the pilot line of the integrated technology for the treatment of Orange/Dioxin

Results of soil washing process for Đ05 on the pilot line of the capacity of 20 kg/h.

Taleb 3: Analysis results of Orange/Dioxin in the products after washing the contaminated soil by surfactant S2 at the concentration of 0.5CMC on the pilot line.

No	Product after washing process	The concentration of contaminants after washing process				
		2,4D (ppm)	2,4,5T (ppm)	2,4DCP (ppm)	2,4,5TCP (ppm)	2,3,7,8 TCDD (ppt TEQ)
1	Course sand(0,5 < d <2,0mm)	0.31	1.22	0.008	0.05	189.93
2	Small sand(0,1< d < 0,5mm)	0.39	1.06	0.009	0.07	575.82
3	Fine sand(0,075< d< 0,1mm)	1.39	1.69	0.008	0.09	1020.87
4	Slit/clay(d< 0,075mm)	85.85	197.34	0.42	1.91	65,423.56
5	Surfactant solution after washing process	10.45	11.28	0.67	0.95	8,686,98
6	D05 (Original)	69.56	117.24	1.53	5.62	22,242.69

Based on the table 3, products of diameter larger than 0.075mm, which account for 77.6% by weight of Đ05 original samples, have inconsiderable concentration of Orange/Dioxin (based on the standard of Vietnam QCVN 45:2012/BTNMT) and possible to return to the environment without requiring any further treatment. The solution after washing process and silt/clay that have very high concentration of Orange/Dioxin should be further treated to meet requirements.

The treatment efficiency of Orange/Dioxin in soils and surfactant solution by nano Fe^0

The solution of nano Fe^0 and activated carbon AC_4 have been used as a chemical agent and an adsorbent. Results of experiments on the treatment efficiency of nano Fe^0 and activated carbon AC_4 on Orange/Dioxin in the contaminated soil and in the surfactant solution by have been studied. The treatment efficiency of nano Fe^0

and activated carbon AC_4 depends on many factors. Experiments shows that dosage of nano Fe^0 increases, the treatment efficiency reaches approximately 68.6%, 57.2% and 55.7% (sequentially 2,4-D, 2,4,5-T and 2,3,7,8-TCDD) at the concentration of nano Fe^0 of 50mg/l. The treatment efficiency also depends on the reaction time that is at least 2 hours based on experiments. Besides, pH also has effect on the efficiency, in the range of pH from 2 ÷ 3, the efficiency is the highest and reaches from 68.6% to 70.12%.

Treatment of Orange/Dioxin by thermal desorption in the presence of catalysts.

Activated carbon AC_4 that has been used to adsorb Orange/Dioxin and separated from silt/clay by floating process is thermally treated in the presence of catalysts. The presence of nano CaO/Fe_3O_4 promotes the decomposition of Orange/Dioxin with higher efficiency at lower temperature. Analysis results show that there is a clear change of thermal decomposition efficiency of Orange/Dioxin at different conditions.

Tab 4: Thermal decomposition efficiency of Orange/Dioxin in experimented samples at different temperature with and without the presence of catalysts.

Samples	Decomposition efficiency (%)								
	T = 150⁰C			T = 250⁰C			T = 350⁰C		
	2,4D	2,4,5T	Dioxin	2,4D	2,4,5T	Dioxin	2,4D	2,4,5T	Dioxin
Đ05	22.53	30.48	9.34	79.21	61.35	11.65	94.32	90.83	15.88
Đ05+ nano CaO/Fe_3O_4	42.61	40.83	28.32	98.55	75.39	97.84	100	100	99.17
AC_4 + Slit/clay	27.54	32.87	12.96	81.21	80.35	25.63	90.31	86.67	41.26
AC_4+ slit/clay + nano CaO/Fe_3O_4	50.43	54.89	30.57	98.75	97.39	98.21	100	100	99.05

Based on the tab 4, at temperature of 250 to 350°C with the presence of nano CaO/Fe_3O_4, the decomposition of Orange/Dioxin reaches 97.84 to 99.17% to meet the standard accepted limit of treated soils. The application of nano CaO/Fe_3O_4 promotes the complete oxidation of Orange/Dioxin at lower temperature. Especially, Catalysts nano CaO/Fe_3O_4 do not cause the secondary contamination on treated soils.

Conlusion

The integrated technology, which is the combination of soil washing by the surfactant solution and chemical-physiochemical treatment and oxidation at low temperature with the presence of catalysts, could reduce considerably the volume of contaminated soils, requiring the treatment. At the smaller volume, the treatment is easier, more effective and cost-reduced. The complete treatment of Orange/Dioxin is highly effective and meets all requirements of the contaminated sites as a result of the selection of suitable surfactants, combined with using nano Fe^0 as a chemical agent, activated carbon AC_4 as an adsorbent for the pollutants in the solution and nano CaO/Fe_3O_4 as catalysts for thermal treatment. Experimental results show that with the presence of nano CaO/Fe_3O_4 as a catalyst for thermal decomposition of contaminated silt, at temperature of 250 to 350°C and reaction time of 2 hours, the efficiency is 98.68% to 99.17%.

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