Korean J. Chem. Eng., **18**(2), 190-195 (2001)

Adsorption of Basic Dyes in a Fixed Bed Column

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(*Received 27 July 2000 • accepted 9 January 2001*)

Abstract–The adsorption of basic dyes from aqueous solution onto granular activated carbon and natural zeolite has been studied by using a fixed bed column. The design procedures for fixed bed adsorption columns have been investigated for two basic dyes, Maxilon Goldgelb GL EC 400% (MG-400) and Maxilon Shwarz FBL-01 300% (MS-300). The effects of process variables such as bed height, volumetric flow rate, and dye concentration have been investigated. The results have been used to predict the effect of parameter changes on the system by using the bed depth service time (BDST) approach. The performances of the column charged with the natural zeolite were compared with those of the column charged with activated carbon.

Key words: Adsorption, Bed Depth Service Time, Natural Zeolite, Activated Carbon, Basic Dye

INTRODUCTION

The removal of dyes and organics in an economic fashion remains an important problem although a number of successive systems have been developed with adsorption techniques. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, ease of operation, and insensitivity to toxic substances [Meyer et al., 1992].

Activated carbon is the most popular adsorbent and has been used with great success [Walker et al., 1997], but is expensive. Consequently, new materials such as chitin [McKay et al., 1982], silica gel [McKay et al., 1980], wood [Poots et al., 1976], peat [Poots et al., 1976b], natural clay [El-Geundi, 1993a, b], bagasse pith [McKay, 1998] fibers, and polymeric adsorbents [Hwang et al., 1993a, b], are being studied. A very limited amount of information is available on the use of natural zeolites as a method for dye removal [Lin, 1993; Meshko et al., 1998]. For a full description of low cost adsorbents for waste and wastewater treatment, a review has been presented by Pollard et al. [1992].

Fixed bed operations are widely used in pollution control processes such as separating ions by an ion-exchange bed or removing toxic organic compounds by carbon adsorption bed. For an optimal design of an industrial adsorption process it is important to have accurate modelling and simulation of the dynamic behaviour of fixed bed systems to optimise column design and operation. Several models have been developed to predict results for a variety of adsorption systems [Tien, 1994; Ruthven, 1984; Lee et al., 1997]. These models based on fundamental mass transport mechanisms including external film, pore, and surface diffusion have been proposed but require the solution of a number of non-linear partial differential equations which include physical and kinetic parameters. These equations can be solved only by numerical methods that are time consuming and tedious.

By using shortcut models pilot plant testing could be used largely for verification rather than information gathering, saving time and money. The bed service time (BDST) model [Hutchins, 1973] and the mass transfer zone (MTZ) model [Michaels, 1952] offer the simple approach and rapid prediction of adsorber performance. The bed depth service time (BDST) model has been successfully used in describing and predicting dye column adsorption using different adsorbents [McKay et al., 1984; Walker et al., 1997].

The aim of this work is to study the ability of natural zeolite to remove dyes from aqueous solutions. This adsorbent was chosen because of its cheapness and abundance. The BDST model was used to predict the performance of a fixed bed column for adsorption of two basic dyes on natural zeolite and granular activated carbon (GAC). The performances of the column charged with the natural zeolite and the activated carbon were compared.

BED DEPTH SERVICE TIME MODEL

In the fixed bed systems, the main design criterion is to predict how long the adsorbent material will be able to sustain removing a specified amount of impurity from solution before regeneration is needed. This period of time is called the service time of the bed. Hutchins [1973] proposed a simple approach to fixed bed adsorbers to correlate the service time with the process variables:

$$t = \frac{N_o}{C_o v} Z - \frac{1}{k_a C_o} \ln\left(\frac{C_o}{C_b} - 1\right) \quad (1)$$

The model is termed as the bed depth service time (BDST) model. In Eq. (1), t and Z are correlated with the process variables: initial dye concentration, solution flow rate, and adsorption capacity. The theoretical depth of adsorbent sufficient to prevent the adsorbate concentration from exceeding C_b at t=0, named the critical bed depth (Z_o), can be obtained from Eq. (1) when the service time is zero:

$$Z_o = \left(\frac{v}{k_a N_o}\right) \ln\left(\frac{C_o}{C_b} - 1\right) \quad (2)$$

By plotting the service time t against the bed depth Z [Eq. (1)] from experimental data, N_o can be evaluated from the slope of the graph,

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and k_a is obtained from the intercept at t=0, i.e., from the critical bed depth Z_o. The reciprocal of the slope is the rate at which the adsorbent bed is spent, and multiplying this value by the adsorbent's apparent bulk density gives adsorbent usage rate to continuously produce an acceptable product. The BDST model [Eq. (1)] can be written in its simplified form:

$$t=AZ+M \tag{3}$$

where

$$A=\frac{N_o}{C_o v} \tag{4}$$

$$M=\frac{1}{k_a C_o}\ln\left(\frac{C_o}{C_b}-1\right) \tag{5}$$

The slope of the line presented by Eq. (3) can be used to predict the performance of the bed, if there is change in the initial dye concentration C_{o1} to a new value C_{o2}, Hutchins [1973] proposed that the new slope A_2 and new intercept M_2 can be estimated by Eq. (6) and Eq. (7), respectively:

$$A_2=A_1\left(\frac{C_{o1}}{C_{o2}}\right) \tag{6}$$

$$M_2=M_1\frac{c_{o1}\ln[(c_{o2}/c_b)-1]}{c_{o2}\ln[(c_{o1}/c_b)-1]} \tag{7}$$

McKay et al. [1984] stated that if design data are required for a change in volumetric flow rate of solute to the same adsorption system, the new slope with the intercept remaining uncharged can be written as:

$$A_2=A_1\left(\frac{Q_1}{Q_2}\right)=A_1\left(\frac{v_1}{v_2}\right) \tag{8}$$

EXPERIMENTAL

1. Materials

1-1. Adsorbates

Two basic dyes were used as adsorbates: Maxilon Goldgelb GL EC 400% (MG-400) and Maxilon Shwarz FBL-01 300% (MS-300). They were used as commercial salts without purification and were supplied by Ciba-Geigy, Germany.

1-2. Adsorbents

The natural zeolite type ZB was supplied by "Nemetali", Vranjska Banja, SR Yugoslavia. The mineralogical composition of the natural zeolite is 90% clinoptiolite and the rest is mordenite and haylandrite. Prior to an experiment, the natural zeolite was dried at 300 °C for 48 hours in order to remove any traces of moisture or other contaminants. The granular activated carbon (GAC) was supplied by "Miloje Zakic", Krusevac, SR Yugoslavia. Prior to an experiment, GAC was washed and dried at 100 °C for 24 hours. Some of the properties of the adsorbents are listed in Table 1.

Table 1. Properties of natural zeolite and GAC

	Natural zeolite	GAC
Particle diameter, mm	1-3	1.15-1.35
Bed porosity	0.325	0.411
Particle density, g/cm^3	2.12	1.87
Bulk density, g/cm^3	1.43	1.0-1.2
Surface area, m^2/g	20-40	1150-1200

2. Analysis

The concentration of the dyes was measured with a Hach DR/2010 spectrophotometer at a wavelength corresponding to the maximum absorbance for each dye, 450 nm and 600 nm, for MG-400 and MS-300, respectively. In accordance with the Lambert-Beer law the adsorbance was found to vary linearly with concentration and dilutions were undertaken when adsorbance exceeded 0.6.

3. Fixed Bed Experiments

The column tests were carried out in a glass column with an inside diameter of 1.5 cm and height of 15 cm. The adsorbents with known weight were put into the column randomly. The average temperature during the experiments was maintained at 20 °C. In an adsorption column test, an aqueous dye solution was fed to the bottom of the column by a peristaltic pump (AMEX Mastreflex), flowed through adsorbent bed and than exited from the top of the column. The influence of bed height, initial dye concentration, and volumetric flow rate on the breakthrough curves was determined, and the experimental conditions are presented in Table 2.

RESULTS AND DISCUSION

1. Effect of the Bed Height

The adsorption columns used during this study contained sampling ports along the height of the column, which provided access to determine the effect of the bed height on adsorption. The effect of the bed height on the breakthrough curves for some investigated systems is presented in Figs. 1 and 2. The results indicate that the profile of the breakthrough curves varies with bed height. Curves in the lower section of the bed have a concave profile and are close to an "S" profile at the column outlet. These trends indicate that the breakthrough does not follow the characteristic "S" shaped profile produced in ideal adsorption systems, behaviour which is associated with adsorbates of smaller molecular diameter and simpler structure.

The research on the adsorption of dyes [McKay et al., 1984; Walker et al., 1997] shows similar profile. According to Walker et al. [1997] the variation in concentration profile is due to relatively large adsorption zone, i.e., the adsorbent near the top of the column comes into contact with dyes before the adsorbent near the bottom of the column is saturated. The large molecules of dyes need enough con-

Table 2. Experimental conditions of fixed bed column test

Run	Dye	Adsorbent	Initial conc. Co (mg dm^{-3})	Flow rate (cm^3 min^{-1})	Height L (cm)
1	MG-400	GAC	50; 100; 200	40; 65; 100	7.5; 11.3; 15
2	MS-300	GAC	50; 100; 200	40; 50; 65	7.5; 11.3; 15
3	MG-400	Natural zeolite	50; 100; 200	2; 8; 40	7.5; 11.3; 15
4	MS-300	Natural zeolite	50; 100; 200	25; 35; 50	7.5; 11.3; 15

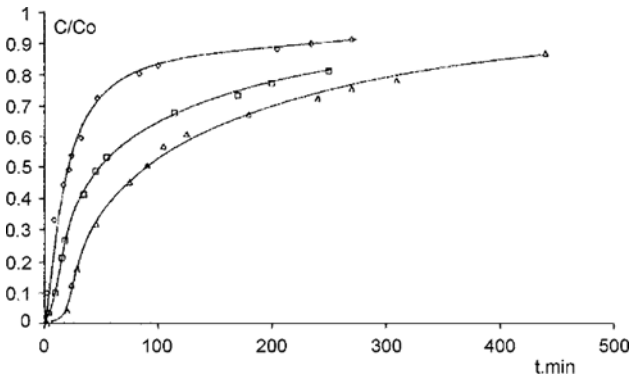

Fig. 1. Effect of bed height on breakthrough curves for the system MS-300 on GAC.
Q=65 cm^3 min^{-1}, c_o=50 mg dm^{-3}
◇=7.5 cm; □=11.3 cm; △=15 cm

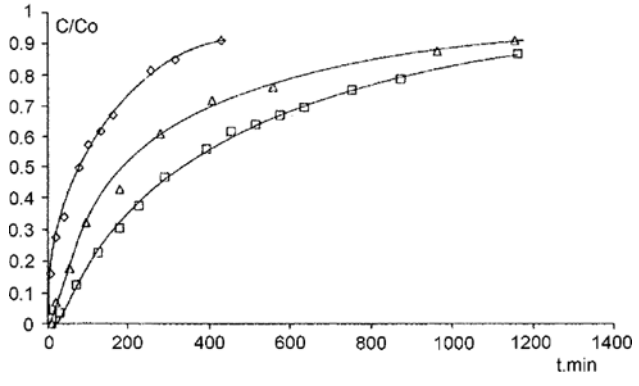

Fig. 2. Effect of bed height on breakthrough curves for the system MG-400 on natural zeolite.
Q=8 cm^3 min^{-1}, c_o=50 mg dm^{-3}
◇=7.5 cm; □=11.3 cm; △=15 cm

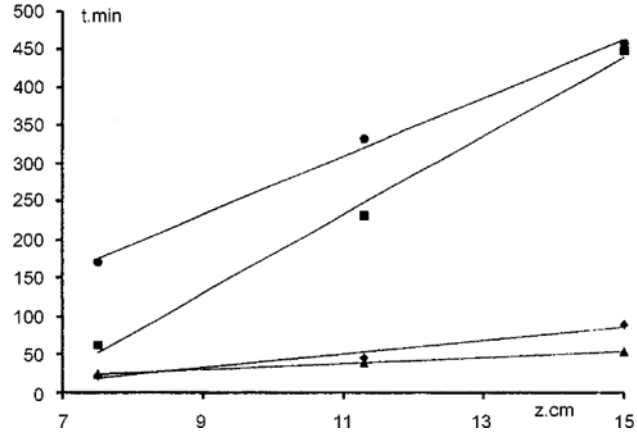

Fig. 3. BDST plots.
◆ MS-300 - GAC, ▲ MS-300 - natural zeolite
■ MG-400 - GAC, ● MG-400 - natural zeolite

tact time to diffuse from the surface of the particle to the adsorption sites; therefore, the column with the higher bed has to be used for these adsorbates.

Using the BDST approach, the relationship between service time and bed depth for the adsorption of MS-300 and MG-400 onto gran-

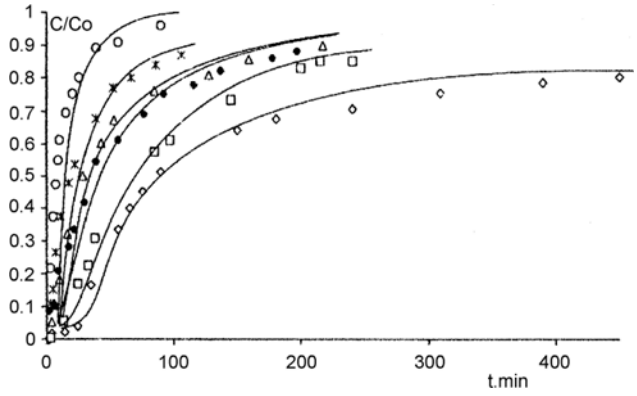

Fig. 4. Effect of initial concentration for the systems.
MS-300 on GAC at Q=65 cm^3 min^{-1}
◇ c_o=50 mg dm^3, □ c_o=100 mg dm^3, △ c_o=200 mg dm^3
MS-300 on natural zeolite at Q=35 cm^3 min^{-1}
● c_o=50 mg dm^3, × c_o=100 mg dm^3, ○ c_o=200 mg dm^3

ular activated carbon and natural zeolite at 50% breakthrough values for various bed depths, is presented in Fig. 3. It can be seen that a linear relationship is established, which confirms Eq. (3).

2. Effect of the Initial Dye Concentration

The initial dye concentration of the effluent is important since a given mass of adsorbent can only adsorb a fixed amount of dye. Therefore, the more concentrated an effluent, the smaller is the volume of effluent that a fixed mass of adsorbent can purify. Several experiments were undertaken to study the effect of varying the initial dye concentration on the rate of dye removal from solution. The breakthrough curves for the systems MS-300-GAC and MS-300 - natural zeolite are presented in Fig. 4.

Effect of initial dye concentration in the inlet flow is one of the limitation factors and main process variables. An increase in the inlet dye concentration increased the slope of the breakthrough curve, reducing the volume treated before adsorbent regeneration. An increased inlet dye concentration at a constant flow rate decreases the throughput until breakthrough. This may be caused by high dye concentrations saturating the adsorbent more quickly, thereby decreasing the breakthrough time.

The BDST constants were calculated from the slope and intercept [Eq. (1)] for all investigated systems and they are presented in Table 3.

Variations in the inlet concentration affected the BDST constants with some trends being established (Table 3). In general, an increase in dye concentration increased the critical bed depth (Z_o) of the adsorption column. The values of the critical bed depth were higher for adsorption of MG-400 and MS-300 on GAC than on natural zeolite. On the other side, the critical bed depth for MG-400 was higher than for MS-300 for both of the adsorbents used. An increase in dye concentration also appeared to increase the adsorption capacity with this variation being most evident in MG-400. The rate constant k_a did not appear to follow any correlation with the change of c_o.

Altering c_o will change both the slope and the intercept of the BDST plot as indicated in Eq. (5). At a fixed breakthrough and defined operating conditions, the critical bed height will increase when c_o increases, which agrees with the experimental results. The small

Table 3. Effect of dye concentration on BDST parameters

c_o (mg dm^{-3})	Z_o (cm)	N_o 10^{-4} (mg dm^{-3})	k_a 10^4 (dm^3 mg^{-1} min^{-1})	BDST capacity (mg g^{-1})
MS-300-Natural zeolite for Q=50 cm^3 min^{-1}				
50	1.90	0.58	4.5	3.84
100	3.89	0.82	4.5	5.43
200	4.36	0.80	4.6	5.29
MS-300-GAC for Q=65 cm^3 min^{-1}				
50	5.48	1.66	1.9	19.1
100	7.00	1.72	1.7	19.8
200	8.01	1.73	1.2	19.9
MG-400-Natural zeolite for Q=8 cm^3 min^{-1}				
50	2.96	0.87	1.1	5.76
100	7.13	1.20	0.8	7.94
200	7.40	1.25	0.8	8.28
MG-400-GAC for Q=40 cm^3 min^{-1}				
50	6.49	5.87	0.89	67.6
100	8.97	5.87	0.70	67.6
200	9.16	5.90	0.90	67.9

Table 4. Effect of flowrate on BDST parameters

Q (cm^3 min^{-1})	Z_o (cm)	N_o (mg dm^{-3})	k_a (dm^3 mg^{-1} min^{-1})	BDST capacity (mg g^{-1})
MS-300-Natural zeolite for c_o=50 mg dm^{-3}				
25	1.80	1.20	10	7.94
35	2.14	1.00	11	6.62
50	1.90	0.58	4.5	3.84
MS-300-GAC for c_o=50 mg dm^{-3}				
40	3.90	1.82	2.5	20.9
50	4.88	1.79	1.1	20.6
65	5.48	1.66	1.0	19.1
MG-400-Natural zeolite for c_o=50 mg dm^{-3}				
2	0.95	1.00	2.2	6.62
8	2.96	0.87	1.1	5.76
40	3.75	1.05	5.4	6.95
MG-400-GAC for c_o=50 mg dm^{-3}				
40	6.49	5.87	0.89	67.6
65	8.00	5.60	1.10	64.5
100	9.80	5.60	1.99	64.5

deviation from prediction, which will arise, may be caused by the fact that the BDST theory is based on the Bohart/Adams equation, which assumes a rectangular isotherm. The isotherms for all investigated systems are favourable, not step function in shape [Meshko et al., 1999].

3. Effect of Volumetric Flow Rate

In the design of a fixed bed adsorption column, the contact time is the most significant process variable: therefore, bed depth and dye flow rate are the major design parameters. The effect of varying the volumetric flow rate was investigated for the two dyes and two adsorbents. The breakthrough curves for MS-300 onto granular activated carbon and natural zeolite are presented in Fig. 5.

From Fig. 5 it is obvious that an increase in flow rate decreases the volume treated until breakthrough and therefore the service time of the bed. This is due to decreased contact time between the dye and the adsorbent at higher flow rates. When the flow-rate has smaller values, equilibrium correspondent with batch experimental data could be reached, and the shape of the curves is more like an ideal breakthrough curve, or that critical value of outlet concentration is moved to theoretical one close to 90% of inlet concentration.

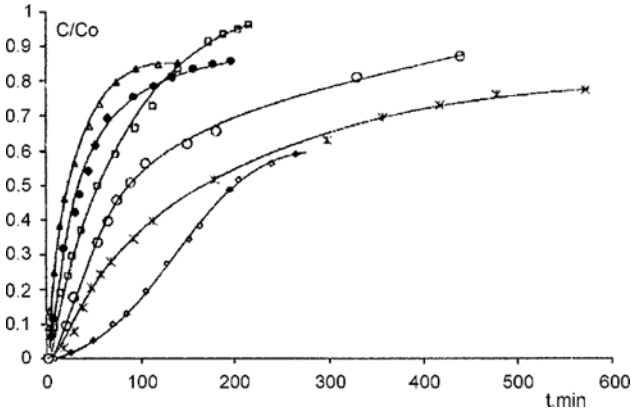

Fig. 5. Effect of volumetric flow rate for the systems.
MS-300 on GAC at c_o=50 mg dm^{-3}
○ Q=65 cm^3 min^{-1}, × Q=50 cm^3 min^{-1}
MS-300 on natural zeolite at c_o=50 mg dm^{-3}
◇ Q=10 cm^3 min^{-1}, □ Q=25 cm^3 min^{-1}, ● Q=35 cm^3 min^{-1}, △ Q=50 cm^3 min^{-1}

For the same flow rate the contact time is smaller for the systems dye-natural zeolite than for the systems dye-GAC.

The BDST constants were calculated by the same procedure as already given in the previous section and they are presented in Table 4.

For both dyes, the critical bed depth (Z_o) showed an increase with the increase in the flow rate. The values of the critical bed depth were higher for adsorption of MG-400 and MS-300 on GAC than on natural zeolite. At the same time, the critical bed depth for MG-400 was higher than for MS-300 for the both adsorbents used. Calculated values of the adsorption capacity (N_o) and BDST capacity in general showed a decrease with increasing flow rate. However, the rate constant k_a did not show consistent trends for variation in flow rate in these systems. The rate parameter k_a is dependent on the effect of both external film diffusional mass transport, which varies with fluid velocity, and interparticle diffusion, which is independent of fluid velocity. The experimental results show that the slope changes with flow rate, but the significance of this dependence varies from system to system. The dependence demonstrates that both interparticle diffusion and external film diffusion are important rate determining factors in the dye adsorption system, and therefore the k_a value will be affected by the change in velocity.

4. Effect of Dye and Adsorbent Type

The BDST capacity in milligrams per gram for each dye and adsorbent type was calculated from fixed beds operated under identical process conditions of flow rate, and initial concentrations for both dyes are presented in Table 5.

Table 5. Effect of dye and adsorbent on BDST capacity

Dye	Adsorbent	Equilibrium capacity (mg g^{-1})	BDST capacity (mg g^{-1})	Fraction of equilibrium (%)
		c_o=50 mg dm^{-3} Q=50 cm^3 min^{-1}		
MS-300	Natural zeolite	55.86	3.84	6.87
MS-300	GAC	309.20	20.60	6.67
		c_o=50 mg dm^{-3} Q=40 cm^3 min^{-1}		
MG-400	Natural zeolite	14.91	6.95	46.7
MG-400	GAC	159.00	67.60	42.5

MG-400 and MS-300 being adsorbed onto granular activated carbon, have equilibrium capacity of 159.00 mg g^{-1} and 309.2 mg g^{-1}, respectively. Natural zeolite has lower saturation capacities for MG-400 and MS-300, namely 14.91 mg g^{-1} and 55.86 mg g^{-1}, respectively [Meshko et al., 1999]. For both adsorbents the equilibrium capacities for MG-400 are lower than for MS-300, because the molecules of MG-400 are more branched out and its molecules are probably unable to penetrate into the pores in which the molecules of MS-300 can penetrate easily. The higher adsorption capacity for both dyes for the granular activated carbon in comparison to the natural zeolite, might be due to the high pore fraction capable to adsorb the dye molecules. The pores of the natural zeolite are with strong defined size, and that is the reason why the large dye molecules cannot penetrate inside the pores. So a large part of the available surface for adsorption of the natural zeolite is unused.

The overall adsorption capacity of the bed expressed as BDST capacity is significantly less than equilibrium capacity (Table 5). This is more evident for the systems MS-300 - GAC and MS-300 - natural zeolite. BDST capacity expressed as a fraction of the equilibrium capacity indicates differences between each of the dye types. The values of the fraction of equilibrium for MG-400 exceed 40%, while for MS-300 are about 6-7%. This observation leads to the conclusion that the adsorption process of MS-300 is internal diffusion controlled more than adsorption of MG-400.

A detailed investigation of the molecular size of both dyes, characteristics of adsorbent surface, and adsorption kinetics is needed for completely defining the rate controlling mechanism.

CONCLUSION

The adsorption of basic dyes onto granular activated carbon and natural zeolite in a fixed bed column was studied. The experimental results showed that both adsorbents removed the dyes effectively, and the effect of changing the column operating variables, such as flow rate and initial concentration, can be predicted by the BDST model. The breakthrough curves calculated from the adsorption of basic dyes onto both adsorbents indicate that the dye removal is strongly dependent on the kinetics.

The BDST approach is a useful tool for comparing the performance of beds operating under different process variables. The relationships proposed to predict the effect of these parameters gave reasonable approximations to experimental results.

NOMENCLATURE

A : slope of the BDST plot [Eq. (3)] [min m^{-1}]
c_o : initial dye concentration [mg dm^{-3}]
c_b : breakthrough adsorbate concentration [mg dm^{-3}]
k_a : BDST adsorption rate constant [dm^3 mg^{-1} min^{-1}]
M : intercept of abscissa in BDST plot [min]
N_o : adsorption capacity in BDST model [mg dm^{-3}]
Q : volumetric flow rate [cm^3 min^{-1}]
t : time [min]
v : velocity [cm min^{-1}]
Z_o : critical bed height [cm]
Z : bed height [cm]

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