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Elimination of organic pollutant (Acetic acid) by adsorption on clays in aqueous solution: Kinetic study and adsorption isotherms

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ABSTRACT

Everyone now agrees that our planet goes wrong. She will face a dramatic increase in demand for water in the near future. But if it comes to that today is because of our irresponsible behavior vis-à-vis this nature that we have not adhered to its fair value. Indeed, with technological progress combined with a population growth, water demand has increased. This generating capacity is exceeded due to our releases. Indeed, industrial, agricultural and domestic effluents origin is often responsible for low or non-biodegradable pollutants. Their impact on the flora and fauna is very harmful. The elimination of these pollutants can be achieved by adsorption of materials cost, research has focused on the adsorption of acetic acid on clays. Studies in "batch method" were used to determine the contact time (1 hour for the yellow clay with removal efficiency of 41.25% and 2 hours for the gray clay with 35% elimination substrate at a concentration of 0.2 mol / l). However improving the removal efficiency can vary under the influence of some parameters: temperature, concentration of adsorbate in solution, time, mass of adsorbent and pH revealed a significant improvement in capacity and the rate of adsorption of acetic acid on the media. In addition, the adsorption of this compound is well described by kinetic models of Langmuir and Freundlich. As the adsorption kinetics is well described by the model pseudo-second order model. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Organic molecule;
Acetic acid;
Temperature;
pH;
Isotherm;
Kinetic model;
Gray clay and yellow clay.

INTRODUCTION

The intensive use of organic molecules in everyday life has caused problems both in the environment and in food^[1,2]. It is important to mention that environmental pollution is due to discharges of textile industries and in power, the toxicity is due to the incorporation of several organic molecules due to the use of fertilizers and pesticides^[3].

To remedy this situation, several decontamination

methods have been developed, we include for example: adsorption^[4,5], ion exchange^[6,7], flocculation-coagulation^[8]... etc..

In this work, we present the results for the adsorption of acetic acid on two types of clay. To do this, we determined successively, the contact time, the influence of parameters such as temperature, concentration of adsorbate in solution, pH and mass media. This study is essential to understand the mechanisms governing the adsorption

MATERIALS AND METHODS

The clays used are the agadir region.

Measures the concentration of the organic molecule solutions at different reaction times were followed by chemical assay.

The experiments were conducted in “batch method” (in a single flask of 50 ml) at room temperature (25 °C). It should be noted that the temperature control was done by simply reading the thermometer. Also to ensure good dispersion of solid particles, we adopted the value of 10 g/l (0.5 g/50ml) for the solid/ liquid ratio.

The adsorption kinetics was studied using pseudo-first-order model and pseudo-second-order.

As against the study of adsorption isotherms was performed using models of Langmuir and Freundlich.

RESULTS AND DISCUSSION

Characterization of samples of clays

We conducted a mineralogical and elemental analysis to identify two types of clay soils used in our experiments, and an analysis by X-ray:

TABLE 1 shows that 1 and 2 soils are rich in SiO₂ due to the presence of quartz, we also note the presence of CaO and loss of fire respectively 24.81% and

TABLE 1: Results of analysis of clay soils by fluorescence X.

Components	Soil 1	Soil 2
SiO ₂	30,24	34,03
Al ₂ O ₃	10,22	12,13
Fe ₂ O ₃	4,06	4,60
CaO	25,42	20,12
MgO	1,70	2,77
SO ₃	0,04	1,17
K ₂ O	1,25	1,57
Na ₂ O	0,16	0,08
P ₂ O ₅	0,10	0,11
Cl	0,00	0,00
Loss of fire	24,81	22,26
total	98,00	98,84

22.26%. Also, we have significant rates of oxides Fe₂O₃, Al₂O₃, MgO and K₂O.

As Figures 1 and 2 show that 1 and 2 soils are rich in quartz, calcite and chlinochlore characteristic of clay minerals.

So soils 1 and 2 are clays. But to differentiate better, we made a mineralogical analysis for both soils

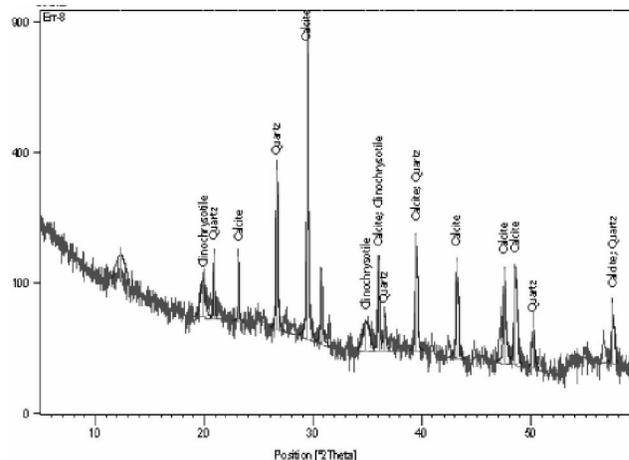


Figure 1: X-ray diffractogram of the soil 1

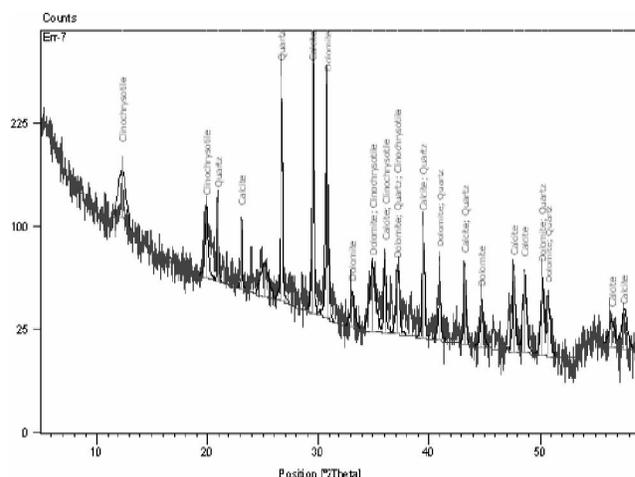


Figure 2: X-ray diffractogram of the soil 2

TABLE 2 : Results of mineralogical analysis of clay soils.

Minerals %	Sol 1	Sol 2
Dolomite %	0	26
Quartz %	26	30
Calcite %	56	32
Clay %	18	12

(TABLE 2), we can conclude that the ground one is yellow clay and soil 2 is gray clay.

Influence of some parameters on the adsorption:

Contact time

The study of the adsorption of acetic acid on yellow and gray clay clearly implies the determination of the con-

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tact time, time which corresponds to the adsorption equilibrium or a state of saturation of the support substrate. In this case, the experimental procedure is simple "batch method", is to be contacted separately, 0.2 mol/l acetic acid with 10 g/l of each soil type. Analysis by chemical assay will determine the residual concentration of said substrate during the samples taken at different reaction times. Thus the determination of the equilibrium time, led to the establishment of adsorption isotherms that are essential for the calculation of the maximum adsorption capacity and to identify the type of adsorption to occur in single or multi-layer. The results from Figure 3 showed that the contact time obtained is 2 hours for the two types of clay with a

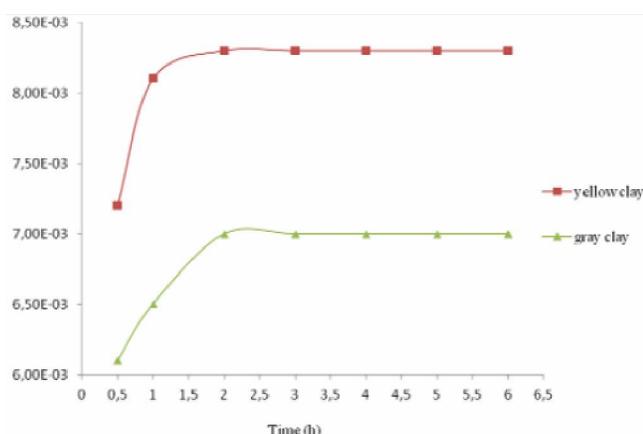


Figure 3 : Influence of the contact time on the acetic acid adsorption

removal efficiency of the organic molecule of 41.25% for the yellow clay and 35 % for gray clay.

Moreover, the extension of the time until 6 hours does not lead to a further improvement. This justifies the inclusion of this contact time for other adsorption experiments. This result was obtained by the relation^[9]:

$$Q = \frac{(C_0 - C_t) * V}{m}$$

Q: adsorption capacity of the support (mg/g); C₀: initial concentration of organic molecule (mg/l) at t=0; C_t: Concentration of the organic molecule (mg/g) at time t of the adsorption process; V: Volume of solution (substrate) (liter); m: Mass of support (g).

Other factors such as the initial concentration, temperature, pH and adsorbent mass may influence the adsorption capacity^[10]. In addition, it finds its application in various adsorption models used

Influence of the initial concentration and temperature

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Examination of Figures 4 and 5 shows the influence of the initial concentration on the adsorption capacity of the organic molecule (the mass of the support being fixed). We note that it grows along with the increase in initial concentration. According to the classification of Giles (1960), these curves have the shape of the S type where the solute is in competition with the solvent for the occupation of binding sites present on the solid phase. These curves are characteristic of monofunctional organic molecules with

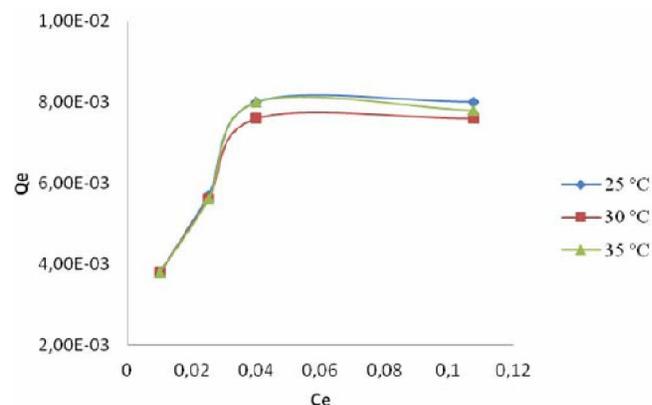


Figure 4: influence of temperature and the initial substrate concentration on the adsorption of acetic acid on the clay yellow

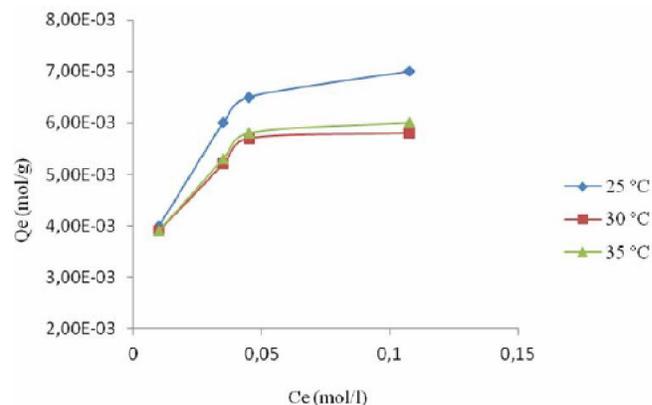


Figure 5 : Influence of temperature and the initial substrate concentration on the adsorption of acetic acid on the clay gray

moderate intermolecular attractions.

But the temperature, the experimental results show a strong retention for low temperatures and shows that this parameter affects negatively the process by high energy contribution to increasing the repulsive forces located at the interfaces of solid and liquid media^[11]. So it is interesting to note that the contribution of heating plays a direct role in the kinetics of retention of the organic molecule. This means that the retention process can be exothermic

($\Delta h < 0$) and in these conditions lead to a physisorption^[12].

Influence of pH

From Figure 6, we find that the adsorption is highly dependent on pH for both soil types, we note. Increasing the amount adsorbed with increasing pH., The adsorbed amount increases to a maximum at pH = 5.5 for yellow

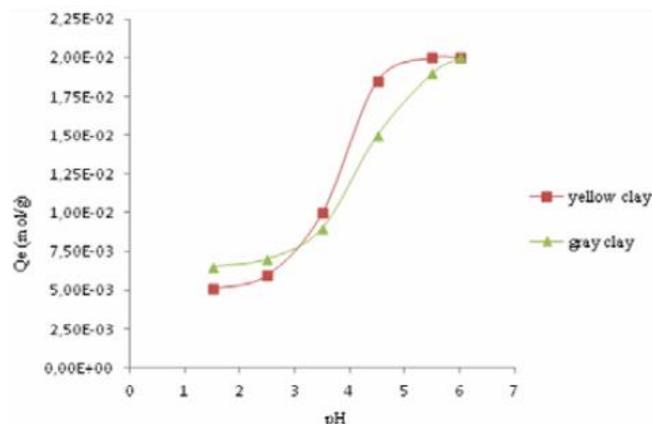


Figure 6 : Influence of pH on the adsorption of acetic acid

clay and pH = 6 for the gray clay.

The adsorption is much better for the environment slightly acidic pH < 4.5.

Probably as acetic acid is stable to the acidic media and basic media, the anionic form of acetic acid (acetate) and becomes stable thereafter promotes adsorption

Influence of the mass of adsorbent

Figure 7 illustrates the variation of the amount adsorbed from the masses of adsorbents used at an ambient temperature of 25 ° C. Indeed, we observe that the adsorbed amount of acetic acid increases with increasing mass. The optimal mass of clay is 1.5 g against

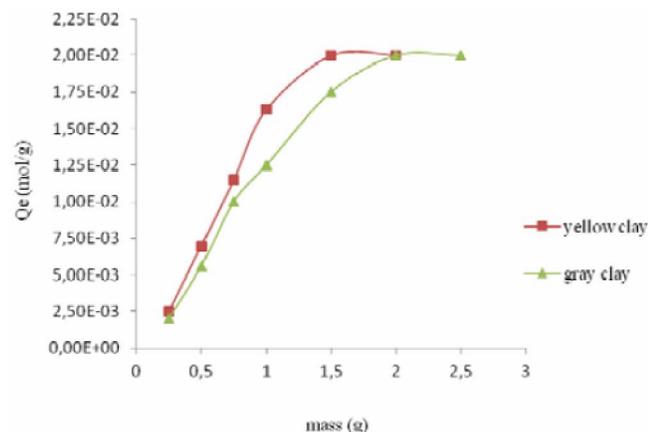


Figure 7 : Influence of the mass of adsorbent in the adsorption of acetic acid

it is 2 g for gray clay.

Study of adsorption isotherms

The adsorption isotherms are important in determining the maximum capacity and identifying the type of adsorption. They are obtained first, by the knowledge of contact time and then the graphical representation of $Q_e = f(C_e)$ where Q_e and C_e are respectively the amount of the organic molecule adsorbed per gram of adsorbent and concentration the balance of the organic molecule, respectively. The experimental results show that the isotherm is of type L, which corresponds to the classification of Gilles^[13]. This indicates a growth of adsorption when the concentration of the adsorbate increases, and these curves can be mathematically described by the Langmuir equation or Freundlich (see below). As the number of sites occupied by solute molecules increases, the adsorption of new molecules become difficult. The molecules are arranged in a monolayer on the solid surface. The shape obtained shows that the adsorption of the organic molecule process could occur in monolayer. Because of their simplicity, the kinetic models, the most commonly used are those of Langmuir and Freundlich.

Langmuir isotherm: is represented by the following equation:

$$Q_e = \frac{Q_0 a C_e}{1 + a C_e}$$

Q_e : Quantity adsorbed at equilibrium per unit weight of the adsorbent (mg/g); Q_0 : adsorption capacity at saturation (mg/g) and correspond to the formation of a monolayer; a : adsorption coefficient.

The linearization of the Langmuir equation determines the parameters a and Q_0 .

Representing

$$\frac{1}{Q_e} = \frac{1 + a C_e}{Q_0 a C_e} = \frac{1}{Q_0 a C_e} + \frac{1}{Q_0}$$

Representing

$$\frac{1}{Q_e} = f\left(\frac{1}{C_e}\right)$$

We can thus deduce: Q_0 from the intercept. a from the slope.

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TABLE 3 : summarizes the various correlation coefficients obtained for the two models of Langmuir and Freundlich:

Isotherm	Temperature	R ²		
		25 °C	30 °C	35 °C
Langmuir	Clay yellow	0,9457	0,9608	0,9649
	Clay gray	0,9223	0,8848	0,9036
Freundlich	Clay yellow	0,7117	0,7754	0,8036
	Clay gray	0,9978	0,9851	0,9898

Freundlich isotherm: it can be described by the following equation

TABLE 3: Correlation coefficients at different temperatures for the yellow and gray clay

$$Q_e = K_f C_e^{1/n}$$

K_f and $1/n$ are respectively the adsorption capacity in mg/g and a constant indicating the intensity of the adsorption:

$$\ln Q_e = f(\ln(C_e))$$

The linear form of this equation allows the determination of K_f and $1/n$

Representing:

$$\ln Q_e = \ln k_f + \frac{1}{n} \ln C_e$$

Figures 8, 9, 10 and 11 respectively represent Langmuire you Freundlich isotherms at different temperatures:

We can conclude that the adsorption of acetic acid on the yellow clay follows the Langmuir model with a correlation coefficient of 0.9649 at a temperature of 35 °C, for against the gray clay is modeled with Freundlich

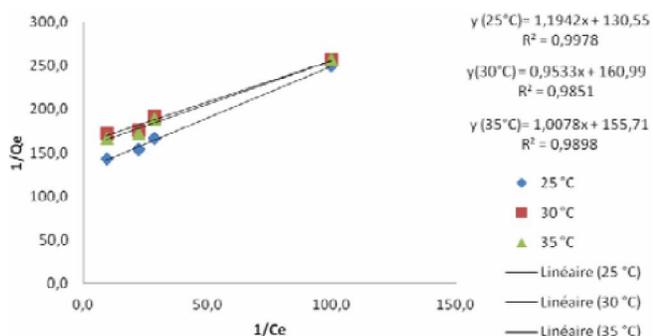


Figure 8 : Langmuir adsorption isotherm for gray clay (25 °C, 30 °C and 35 °C)

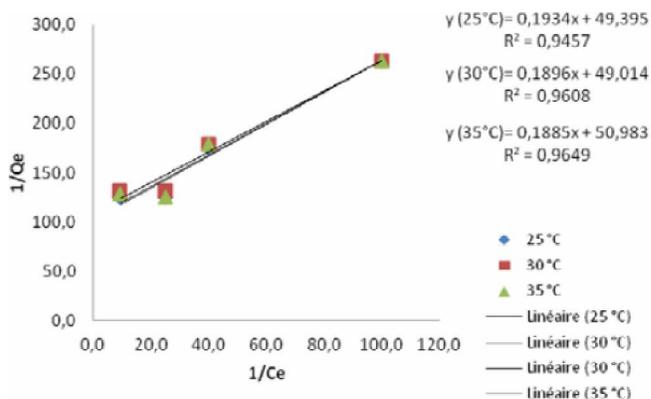


Figure 9 : Langmuir adsorption isotherm for the yellow clay (25 °C, 30 °C and 35 °C)

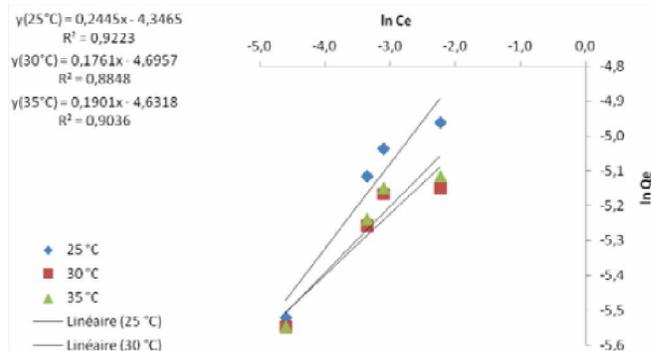


Figure 10 : Freundlich adsorption isotherm for the gray clay (25 °C, 30 °C and 35 °C)

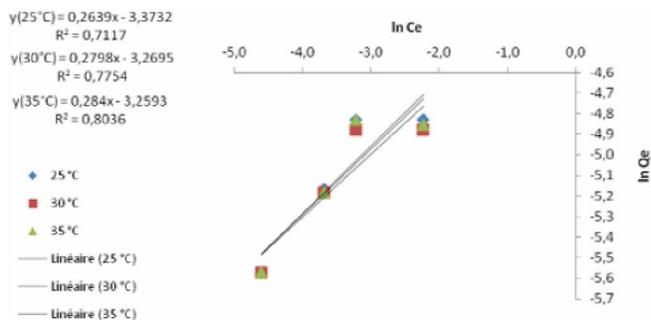


Figure 11 : Freundlich adsorption isotherm for the yellow clay (25 °C, 30 °C and 35 °C)

a correlation coefficient of 0.9978 at a temperature of 25 °C.

So for yellow clay the adsorption energy is constant and independent of the covered surface adsorption is localized sites and it is limited to a monolayer.

Specific area

The specific surface area of an adsorbent is based on measurements of adsorption capacity for a given solute. The adsorbate must have an acceptable surface for the focus to the interior of the pores.

Just donated to determine the value of the monolayer adsorption capacity from adsorption isotherm. Knowledge of the maximum adsorption (mg/g or mol/g) quantity, leading to the determination of σ by the relation:

TABLE 4 : Value Q_0 , K_f , $1/n$ and σ adsorption of acetic acid on the gray and yellow clay

		Clay gray	Clay yellow
25°C	Q_0 (mol/g)	0,007	0,0078
	K_f	0,0130	0,0343
	$1/n$	4,090	3,789
	σ (m ² /g)	885	986
30°C	Q_0 (mol/g)	0,0058	0,0076
	K_f	0,0091	0,0380
	$1/n$	5,679	3,574
	σ (m ² /g)	733	961
35°C	Q_0 (mol/g)	0,006	0,008
	K_f	0,0097	0,0384
	$1/n$	5,260	3,521
	σ (m ² /g)	759	1012

TABLE 5 : Shows the parameters from the pseudo-second order kinetic model :

	pseudo second order					
	C mol.l-1	q_e ,exp (mg.g-1)	q_e ,cal (mg.g-1)	k_2 (min-1)	h_0 (mg g-1 min-1)	R^2
Clay yellow	0,2	0,0083	0,0084	2648,79	0,1861	0,99
Clay gray	0,2	0,007	0,0071	2169,26	0,1093	0,99

the adsorption rate constant (min-1). The values of k_1 and q_e result of the slope and intercept of the plot $\ln(q_e - qt)$ versus t .

Linearised form of the equation of the second order is pseudo^[16]:

$$t/qt = 1/K_2 q_e^2 + t/q_e$$

Where k_2 is the constant rate of adsorption (mg.g-1.min-1).

The equilibrium adsorption capacity, q_e and pseudo-second-order rate constant, k_2 the result from the slope and intercept of the curve t/qt versus t . Figure 5: Parameters of pseudo-second order model for yellow and gray clay. Based on these results, the adsorption of acetic acid on yellow and gray clay is best described by the pseudo-second order model with a correlation coefficient of 0.99.

CONCLUSION

$$\sigma = Q_0 * s * N$$

Where N is Avogadro's number $s = 21 \text{ \AA}^2$ is the area occupied by a molecule of acetic acid.

The specific surface areas obtained at different temperatures are summarized below in TABLE 4: Based on these results in TABLE 4, the adsorption of acetic acid on the yellow clay provides better performance at a temperature of 35 °C with an optimum surface area of 1012 m² / g. Gray clay for the specific surface area is 885 m² / g at a temperature of 25 °C.

Adsorption kinetics

For the adsorption kinetics of acetic acid on both types of clay was studied by adjusting the experimental data with two kinetic models, namely pseudo-first order and pseudo-second order. The form of the equation linearised pseudo-first-order^[16] is generally expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Where q_e and q_t is the amount of solute adsorbed at equilibrium and at time t , respectively (mg.g-1), k_1 is

The results obtained in this work have shown that acetic acid is adsorbed well on the yellow clay of gray clay with the same time and higher removal efficiency for the same mass adsorption on acid yellow clay is better compared with that of gray clay.

The temperature has a positive effect on the gray clay and negative on the yellow clay.

As the acid ph has a negative impact on the adsorption kinetics of the organic molecule to the two types of clay.

The adsorption of acetic acid on the yellow clay follows the langmuir model and the gray clay is well described with the freundlich model

The yellow clay has a surface area greater than that of the gray clay.

The adsorption kinetics is best described by the pseudo-second order model.

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