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Removal of heavy metals from aqueous solution by bentonite

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ABSTRACT

The adsorption onto bentonite of three heavy metals often found in industrial effluents (chromium, iron and zinc) was studied. The kinetic equilibrium data show that the bentonite fixes more chromium (VI) than iron (II) and zinc (II). The adsorption capacities of heavy metals in equilibrium with the bentonite are influenced by the stirring speed and environment temperature. The thermodynamic parameters obtained indicate that the adsorption of heavy metals onto bentonite is a spontaneous and exothermic process.

KEYWORDS

Adsorption;
Bentonite;
Chromium;
Iron;
Zinc.

INTRODUCTION

Industrial activity in the extraction sector or the development of heavy metal generates acqueous effluents containing toxic metal elements in various concentrations, released sometimes without any further treatment in the environment. Thus, water pollution by heavy metals is now a great concern about the water quality and the environment. So it is important to seek ways of more severe treatment of industrial wastewater before their discharge into the natural environment. Metals are toxic in the form of free ions by enzyme inhibition. These metals are more or less easily absorbed through the lungs or gastrointestinal[21]. Cases of acute poisoning occur mainly in the industrial setting and have most often broncho-pneumonia and gastro-intestinal short-term effects[1]. Heavy metals concentrate progressively in the liver kidney, pancreas or testes and can be easily removed if the source of poisoning ceases[20]. The toxicity of heavy metals is widely acknowledged; their dangerousness is due to: their non-degradability, their toxicity at low concentrations and tend to accumulate and concentrate in living organs[26].

The removal of heavy metals in industrial wastes has been extensively studied[2,7,8,22,24,27,28]. The methods useds were: oxidation, adsorption on adsorbent materials such as activated carbon or membrane processes have been effective but in most cases very expensive. Research was then directed toward methods of treatment using low cost materials such as agricultural or forestry wastes, wood, clay. More recently, in the field of pollution control, bentonite knows a vast scope for either the degradation of organic compounds, pollutants or their transformation into less dangerous forms. The use of bentonite as adsorbent of organic pollutants and minerals has attracted the attention of many researchers[4,9,16].

Bentonite is a type of clay discovered in 1888 in

Wyoming USA, named Fort Benton[6]. The bentonite clay is classified as rock, its color depends on inorganic compounds and impurities (organic and metal oxide). She is white, gray or slightly yellow[18]. Bentonite is a clay type montmorillonite. The elementary sheet of montmorillonite is formed by an octahedral layer between two layers of tetrahedral (TOT). Si^{4+} ions are located inside a tetrahedron whose vertices are occupied by oxygen atoms. Al^{3+} ions are located inside an octahedron whose vertices are occupied by four oxygen atoms and two hydroxyl ions. The elementary layers are of type 2/1 separated by water molecules and exchangeable cations[19].

MATERIALS AND METHODS

Adsorbent

The bentonite used in our work is extracted from the deposit at Hammam-Boughrara Maghnia (Tlemcen). It has been provided as a finely divides powder (about 54% of the grains have a diameter less than 2 µm) by (ENOF) company, bentonites Maghnia (Tlemcen). The specific surface area measured by nitrogen adsorption at 77 K for bentonite is $23m^2/g$. From an examination of the results of the chemical composition of bentonite has a high content of SiO_2 trend aluminium[5].

Metals used

To prepare solutions of definite concentration of Cr (VI) ion, Fe (II) and Zn (II), the following salts were used: CrO_3, $FeSO_4.7H_2O$ and $ZnCl_2$.

Adsorption kinetics

To determine the kinetics of adsorption of heavy metals on bentonite at 25°C, a volume of 0,3 liters of solution containing a metal concentration of 100 mg/L is brought into contact at t = 0, with 1 g of bentonite and stirred at 400 tours per minute. The pH of the solution is monitored continuously using a pH meter. The quantity of metal adsorbed by the bentonite is determined as follows:

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

Where: qt: the amount of adsorbed metal (mg per gram of bentonite), Co and Ct: are respectively the initial and instantaneous concentrations of metal (mg/ l), V: volume of solution (L), m: mass of the adsorbent used (g).

The adsorption rate constant is derived from the model established by Lagergreen[15] and developed by Ho[13].

For the first order adsorption rate constant kv is given by the relationship:

$$\log\frac{(q_e - q_t)}{q_e} = -\frac{K_v t}{2,3}$$

For the pseudo second order rate constant K 'is given by the following equation:

$$\frac{t}{q_t} = \frac{1}{2K'q_e^2} + \frac{t}{q_e}$$

For the second order rate constant k is given by the following equation:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt$$

Where: qe: amount of adsorbate at equilibrium per gram of adsorbent (mg/g), t : contact time (min), kv, K and k constants of adsorption rate respectively for the first order (min^{-1}), the pseudo second order ($min^{-1}.g/mg$) and the second order ($min^{-1}.g/mg$).

In general, adsorption is accompanied by a thermal process that can either be exothermic ΔH>0 or endothermic ΔH<0. The measurement of heat of ΔH is the main criterion that differentiates chemisorption from physisorption.

The heat of adsorption is given by the Gibbs-Helmholtz relationship[10,14,23]:

$$\Delta G = -RTLnK_c$$

$$\Delta G = \Delta H - T\Delta S$$

$$LnK_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

With:

$$K_c = \frac{C_e}{(C_0 - C_e)}$$

Where: Kc: Equilibrium constant, ΔG: Gibbs free energy (joule/mol), ΔH: enthalpy (joule/mol), ΔS: entropy (joule/mol / K), T: Absolute temperature (K), Co: Initial concentration of adsorbate, Ce: Equilibrium concentration of adsorbate, R: gas constant (8,314 Joule/mol K)

RESULTS AND DISCUSSION

Adsorption kinetics of heavy metals on bentonite

Figure 1 shows that adsorption kinetics of heavy metals on bentonite are qualitatively similar and characterized by a high metal adsorption on bentonite in the first minutes of contact solution-bentonite, followed by a slow increase up to a plateau corresponding to equilibrium. At aquilibrium bentonite fixed more chromium (VI) and iron (II) than zinc (II). The equilibrium time of adsorption of heavy metals by bentonite is variable. The results are summarized in TABLE 1.

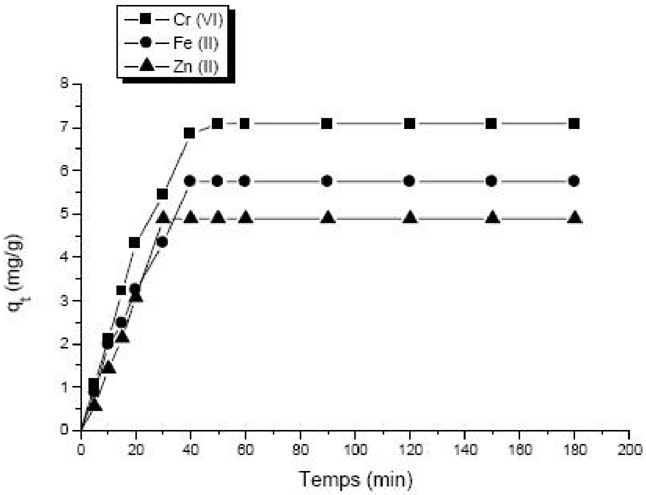

Figure 1 : Adsorption kinetics of heavy metals on bentonite.

TABLE 1 : Results obtained at equilibrium

Metal	Amount of metal fixed at equilibrium (mg/g)	Time of equilibrium (min)
Cr (VI)	7.08	50
Fe (II)	5.74	40
Zn (II)	4.89	30

To explain this order of affinity, we tried to summerize some metals specific parameters for metals involved in their ability to adsorb on bentonite (TABLE 2).

TABLE 2 : Physical properties of heavy metals

Metal	Cr (VI)	Fe (II)	Zn (II)
Atomic mass (g)	52	56	65.39
Atomic radius (A°)	0.35	0.67	0.83
Load	6	2	2

These data may explain easily the better adsorption of chromium ions by bentonite. Due to their smaller size and higher load, they are more easily capted in the bentonite frame work. For the some reasons, iron ions are better adsorbed than zinc one which present the highest atomic radius, atomic mass and the lowest load.

In parallel to the kinetic study of heavy metals adsorption on bentonite, we followed the evolution of the pH of the solutions (Figure 2). For the three heavy metals solutions an increase of the initial pH was observed. The values of TABLE 3 also show that the equilibrium time pH varies for the different heavy metals. This equilibrium time is comparable with that obtained for the kinetics of adsorption of heavy metals by bentonite.

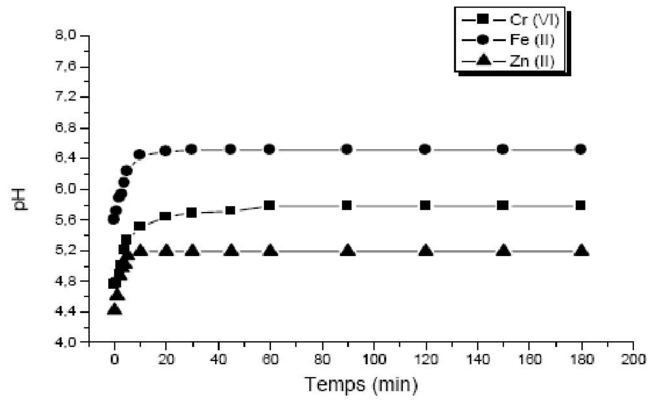

Figure 2 : Evolution of pH of heavy metals in the presence of bentonite

TABLE 3 : pH variation during adsorption of heavy metals on bentonite.

Metal	Initial pH	Equilibrium pH	Time of equilibrium (min)
Cr (VI)	4.75	5.78	60
Fe (II)	5.6	6.51	30
Zn (II)	4.42	5.19	10

The rate constants of adsorption of metals on bentonite for the first and pseudo second order are determined graphically as shown in by (Figures 3, 4 and 5): log $(q_e - q_t)/q_e$ versus time for the determination

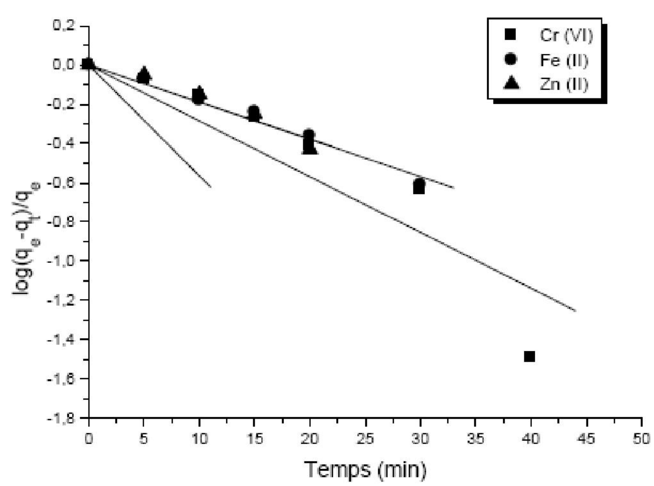

Figure 3 : Determination of rate constants of the first order of adsorption of heavy metals on bentonite.

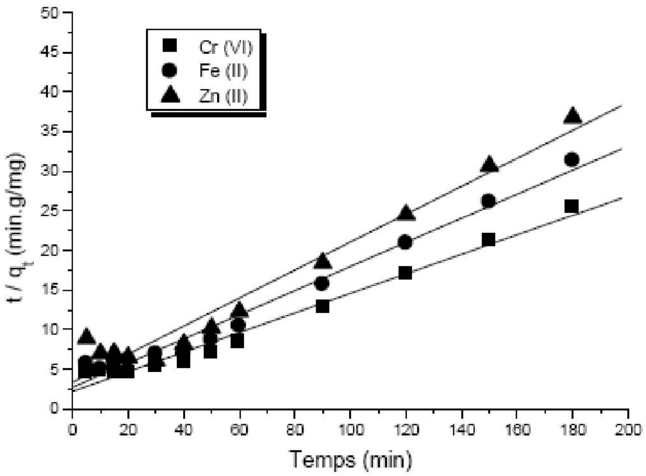

Figure 4 : Determination of rate constants of the pseudo second order adsorption of heavy metals on bentonite.

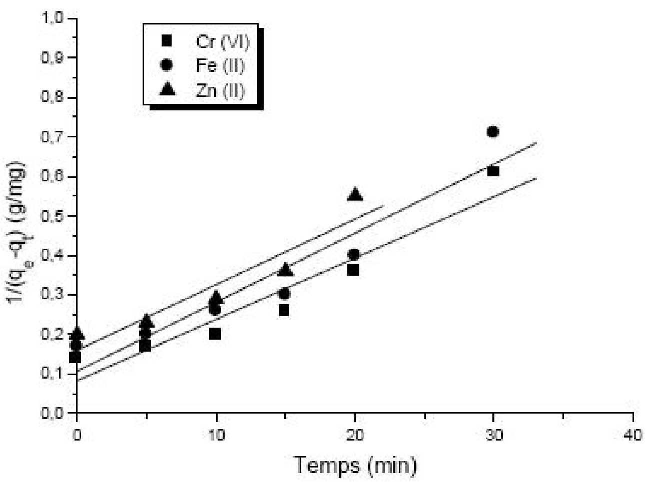

Figure 5 : Determination of rate constants of second order of the adsorption of heavy metals on bentonite.

of kv, for the first order; t/q_t versus time for the determination of K' for the pseudo second order and $1/(q_e-q_t)$ versus time for the determination of k, for the second order. The results thus obtained are presented in TABLES 4, 5 and 6.

The results with a good correlation coefficient (R^2 = 0.99) detailed on TABLES 4, 5 and 6, show that the pseudo second order model is the most reliable way to determine order of adsorption kinetics of different heavy metals by bentonite. Similarly, and from the values of qe shown in TABLE 7, we note that the values calculated by the pseudo second order model are the most close to those determined experimentally.

Effect of temperature on the removal of heavy metals by bentonite

To study the effect of temperature on the adsorption kinetics of heavy metals by bentonite, the following temperatures: 25, 35, 45 and 55°C were chosen. Figure 6 shows that adsorption capacity of metal at equilibrium decrease when increasing temperature.

TABLE 4 : Constants of first order rate

Metal	K_v (min^{-1})	R^2
Cr (VI)	$6.54.10^{-2}$	0.882
Fe (II)	$4.35.10^{-2}$	0.967
Zn (II)	$4.32.10^{-2}$	0.956

TABLE 5 : Constants speeds pseudo second order

Metal	q_e (mg/g)	K' (min^{-1}.g/mg)	R^2
Cr (VI)	8.10	$3.40.10^{-3}$	0.989
Fe (II)	6.56	$4.24.\ 10^{-3}$	0.991
Zn (II)	5.66	$4.61.\ 10^{-3}$	0.996

TABLE 6 : Constant speed of the second order

Metal	q_e (mg/g)	k (min^{-1}.g/mg)	R^2
Cr (VI)	12.03	$1.55.10^{-2}$	0.969
Fe (II)	9.36	$1.74.\ 10^{-2}$	0.951
Zn (II)	6.25	$1.66.\ 10^{-2}$	0.942

TABLE 7 : Comparison of adsorbed amount of various metals by bentonite, balance between experience and modeling used.

Metal	q_e exp (mg/g)	q_e cal (mg/g) pseudo second order	q_e cal (mg/g) second order
Cr (VI)	7.08	8.10	12.03
Fe (II)	5.74	6.56	9.36
Zn (II)	4.89	5.66	6.25

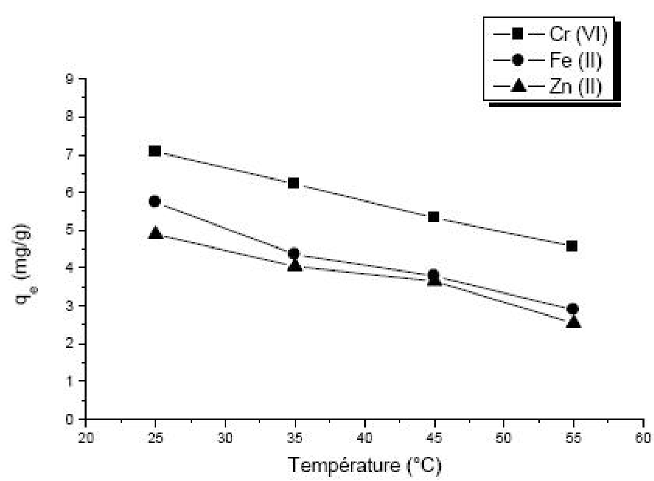

Figure 6 : Influence of temperature on adsorption equilibria of heavy metals on bentonite

The decrease of the amount of adsorbed metals in the temperature range 25-55 ° C, indicates that the adsorption process of chromium (VI), iron (II) and zinc

(II) on bentonite is exothermic. We also note that for the three metals, the temperature did not influence the equilibrium time.

Thus, environmental temperature is an important parameter that can influence the effectiveness of the adsorbent. In general, the increase in temperature weakens the physical or chemical attractive forces. This phenomenon is frequently observed in adsorption reactions[3,11,25].

Determination of thermodynamic parameters of adsorption

The thermodynamic parameters: ΔH and ΔS of heavy metals on bentonite are determined graphically by wearing Ln Kc vs the inverse of the environmental temperature in Kelvin degrees.

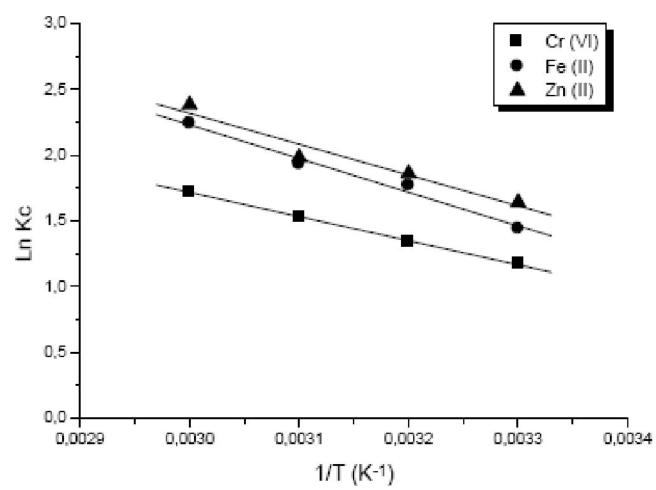

Figure 7 : Determination of enthalpies and entropies of adsorption of metals by heavy bentonite.

From Figure 7, we obtained straight lines with good correlation coefficients, which allows us to calculate Δ H and ΔS for adsorption of heavy metals by bentonite

TABLE 8 : Thermodynamic parameters for adsorption of heavy metals by bentonite.

Metal	ΔH (KJ/mol)	ΔS (J/mol/K)	R^2
Cr (VI)	-15.38	60.48	0.999
Fe (II)	-21.40	82.84	0.984
Zn (II)	-19.56	78.04	0.987

From TABLE 8, the negative values ΔH confirms that the adsorption of heavy metals by bentonite is an exothermic process. Low values of this heat (< 40 KJoule / mol) show that this is a physical adsorption. The positive values of entropy showed that the adsorption of heavy metals by bentonite is accompanied by a disorder of the medium.

Similarly negative values of ΔG data reported in TABLE 9 show that the adsorption of heavy metals on bentonite is a spontaneous process.

TABLE 9 : Gibbs energy of adsorption of heavy metals by bentonite.

Metal	ΔG (K.J/mole) à 25°C	ΔG (K.J/mole) à 40°C	ΔG (K.J/mole) à 50°C
Cr (VI)	-33.40	-34.31	-34.91
Fe (II)	-46.08	-47.32	-48.15
Zn (II)	-42.81	-43.98	-44.76

Effect of stirring speed

To study the influence of stirring speed on the adsorption kinetics of heavy metals by bentonite, the stirring speeds were fixed at 0 rpm (no agitation), 400 rpm (middle agitation) and 900 rpm (stirring up).

The results illustrated in Figures 8, 9 and 10 show that the maximum metal adsorption capacity at equilibrium is obtained with a stirring speed of 400 rpm, which ensures an optimal contact between the different adsorbates and the adsorbent.

Without agitation, we notice a decrease in the adsorption capacity of metal. While for the greater speed of agitation, a very significant decrease in the adsorption capacity of metal is observed.

To explain the effect of this parameter, we can say that in the case of low stirring speeds, the diffusional resistance of the adsorbent is important. While, in the case of high agitation speeds, the grains of the adsorbent

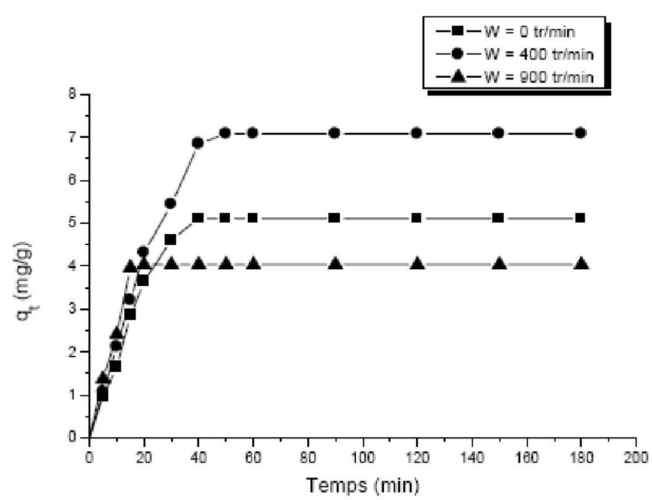

Figure 8 : Effect of agitation speed on the kinetics of adsorption of Cr (VI) with bentonite.

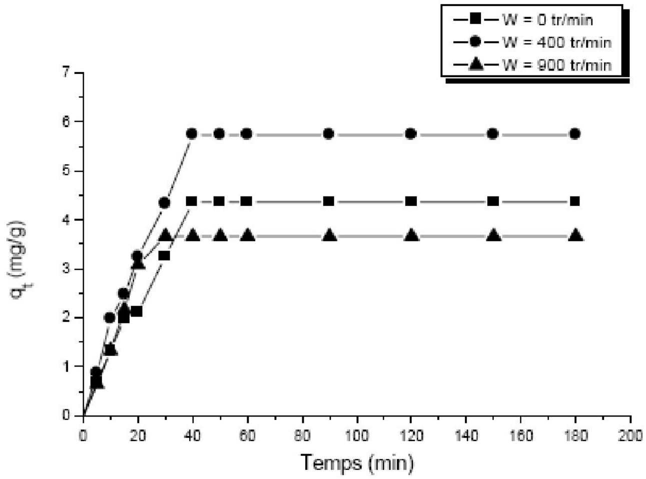

Figure 9 : Effect of stirring speed on the kinetics of adsorption of Fe (II) by bentonite.

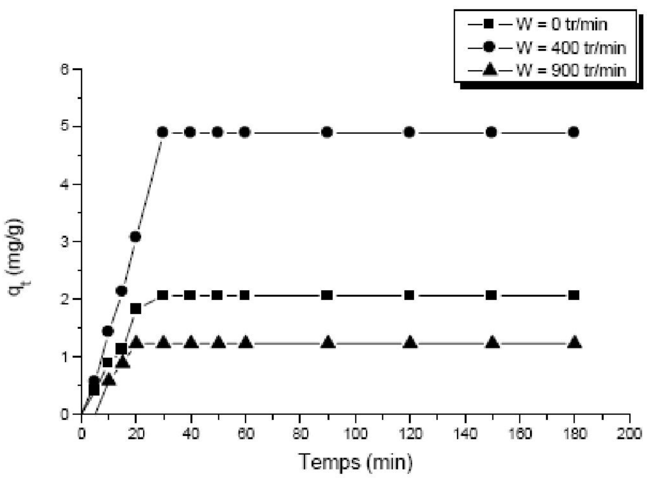

Figure 10 : Effect of stirring speed on the kinetics of adsorption of Zn (II) by bentonite.

are trained and the metal did not have time to settle on the surface of bentonite[12,17].

CONCLUSION

This study was mainly devoted to the study of adsorption capacity of chromium (VI), iron (II) and zinc (II) on bentonite by an inexpensive process to reduce water pollution discharges in a static and dynamic regime. The experiments showed that the studied metals can be adsorbed on bentonite. The affinity of adsorption of heavy metals on bentonite decreases as follows: chromium (VI) > iron (II) > zinc (II). The kinetics of adsorption of heavy metals on bentonite are fast and similar (pseudo second order). The adsorption capacities of heavy metals in equilibrium with bentonite are influenced by the stirring speed and temperature of the medium. The adsorption process is exothermic and spontaneous characterized by a disorder of the medium.

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