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# Removal of Zinc from water by adsorption on different adsorbent

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**Abstract**

The aim of this work is to study zinc removal possibility by adsorption on an Algerian bentonite (bentonite of Maghnia), goethite, powdered activated carbon (PAC) and kaolin. Various reaction parameter effects on process where tested. Experiments were carried out with synthetic distilled water solutions. Kinetic of adsorption results showed that after 20 minutes, zinc removal is maximal with 98.24 % efficiency for bentonite. Using Goethite, we obtained 18% efficiency after 30 minutes of equilibrium time. After 3 hours of stirring, zinc removal by PAC was maximal with 27.54% efficiency and after 1 hour for kaolin with 45.48%. Increasing in adsorbent dose (0.5 to 8 g/l) improves zinc removal efficiency for an initial 5mg/l concentration. Zinc removal efficiency by any adsorbent decreases with the increase of initial zinc concentration (2 to 20 mg/l). pH of treatment affects considerably zinc retention rate. Zn removal efficiencies are noticeable at basic pH. Order of efficiency of tested adsorbents for zinc removal in synthetic solution follows: bentonite > kaolin > PAC > Goethite.

*Keywords:* Zinc, adsorption, bentonite, goethite, powdered activated carbon, kaolin.

## 1. Introduction

Wastewater pollution by heavy metals is a major environmental hazard, since dissolved toxic metal ions may ultimately reach the highest food chain level and become a risk factor for human health. Unlike most pollutants, heavy metals are not biodegradable and tend to accumulate in living organisms causing various diseases [1]. Most commonly cited metals are copper, chromium, nickel and zinc for their numerous industrial applications [2].

In this study, we take the case of zinc is an essential element for all living organisms, including humans and modern life would be inconceivable without zinc, since it plays an essential role in human being metabolism. Major zinc sources in environment are copper and bronze alloys production and galvanization [3,4]. For example, it is vital for more than 200 enzymes correct operation, DNA stabilization, genes expression and signals transmission from nervous system. Human body contains 2 to 3 g of zinc (for 7 g of iron), which are found throughout the body, but with higher concentrations in muscles, liver, kidneys, bones and prostate [5]. It is also used in paints, rubber, plastics, cosmetics and pharmaceuticals [3]. According to International Association of zinc; reduced sensations of taste and smell, skin disorders, mental lethargy and fertility decrease are the main symptoms associated with zinc deficiency in human body.

However, excessive zinc consumption can be toxic and cause nausea, stomach cramps, vomiting, and slow liver dysfunction.... Zinc can also have adverse reactions on environment because it can cause several problems when released in very small quantities, since its toxicity grows by bioaccumulation. Some Algerian studies treated pollution hazards. Natural water reserves in certain regions near industrial areas, for which zinc is in their discharges composition, are contaminated [6, 7].

However, the allowable maximum zinc concentrations in drinking water are 3 to 5 mg/l according to the World Health Organization [8] and 5 mg/l by Algerian standards [9]. In order to meet this standard, several methods have been used to remove zinc as membrane filtration (ultrafiltration, reverse osmosis, nanofiltration, electrodialysis), chemical precipitation, ion exchange and electrochemical method [10]. Adsorption process on clays [11, 12, 13, 14,15,4], on hydroxides [16, 17] and activated carbon

[18, 19] has also proven its effectiveness in laboratory works.

Therefore, the objective of this work is to study bentonite of Maghnia (Algeria), goethite, powered activated carbon powered and kaolin effectiveness for zinc removal from synthetic distilled water solutions.

Many reaction parameters were tested to optimize the process as contact time, effect of adsorbent dose, effect of initial zinc concentration and pH of treatment.

## 2. Materials and Methods

### Solutions of zinc

A 1000 mg/l zinc stock solution was prepared in distilled water and stored away from light, while using zinc sulfate ($ZnS0_4$, $7H_2O$) as salt. Then, we dilute in different ratios to prepare lower solution concentrations used in tests.

### Tested adsorbent

- **Bentonite:** Used clay is a sodic bentonite, white colored, rich in montmorillonite. It is obtained from Hammam Boughrara deposit (Maghnia, N.E of Algeria). This bentonite has acidic pH (pH = 6.2) with a 80 $m^2/g$ specific surface.

**-Goethite :** Used goethite is a FLUKA product. It is an iron hydroxide which chemical formula is Fe(OH)O and specific surface is of 20.5 $m^2/g$.

**-Activated Carbon :** Powdered activated carbon is a DARCO Aldrich lab product, which granulometry is 12 to 20 mesh (0.3 to 0.5 mm) and specific surface is 550 $m^2/g$.

**-Kaolin : It is an Aldrich product which chemical formula is ($Al_2Si_2(OH)_4$), and specific surface is 19.8 $m^2/g$.**

### pH measurement

To measure pH of water samples, a pH meter (HANNA pH 210) was used with a combined electrode (Bioblock Scientific). The pH-meter is calibrated before any measurement series using two buffer solutions of pH 4.01and 9.18.

### Determination of metal concentration

An atomic absorption spectrometer (Shimadzu AA-6200) with hallow cathode lamp and air acetylene flame, was used for determining Zinc concentrations in water samples, at a wavelength $\lambda$ = 213.86 nm.

### Adsorption test description

Zinc removal tests were carried out discontinuously on a magnetic stirrer using synthetic zinc solution contact with a constant mass of each adsorbent.

Solid/liquid sample separation is achieved by vacuum filtration using membrane with 0.45 µm porosity. For each filtered sample, we measured pH and residual zinc concentration.

Several tests were performed to examine some parameters influence on zinc removal on any adsorbent such as stirring time (0 to 6 hr), initial $Zn^{2+}$ content (2 to 20 mg/l), adsorbent dose (0.5 to 8 g / l) and pH of treatment (4 to 9). pH of solutions was adjusted to the desired value by adding HCl (0.1 N) or NaOH (0.1N) during adsorption test.

## 3. Results and discussion

### Kinetics of adsorption

We followed zinc kinetics of adsorption for initial zinc content at 5 mg/l and for both adsorbents constant mass (1g/l). Residual zinc content and pH follow-up were achieved depending on stirring time (from 2 min to 6 hrs).

Obtained results (Fig 1) show that zinc removal efficiency varies with stirring time. We obtained maximum efficiency after 20 min, 30 min, 60 min and 180 min for bentonite, kaolin, goethite and PAC respectively. Maximal removal values corresponding to these times are 98.24 %, 45.48%, 27.54% and 18 % respectively.

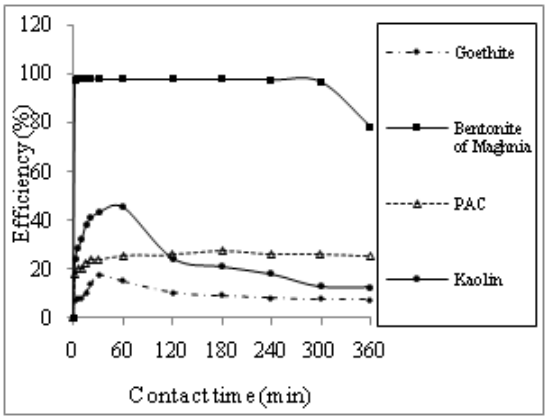


Figure 1: Kinetics curve for Zinc (5mg/l) removal using bentonite, goethite, kaolin and PAC.

Zinc fixation kinetics evolution on clays PAC or hydroxides mainly proved reversibility of exchange engaged and physical nature of adsorbent-zinc interactions.

We can differentiate two steps in zinc kinetics of adsorption for both clays. During first step, we have a rapid efficiency increase, explained by zinc ions quick fixation on both adsorbent surfaces, it is external mass transfer step. Kinetics second step shows that zinc residual content decreases progressively.

Veli and Alyuz [20] tested $Zn^{2+}$ removal, using bentonite of Cankiri (Turkey), prove that pH is an important factor in adsorption process as it generates electrostatic changes in solutions, also showed that equilibrium is reached after very short time (05 min).

Bradl [21], supposed that adsorption mechanisms include ion exchanging (reaction and fixation). Reaction between $Zn^{2+}$ and cation exchangeable at clay surface can be expressed by:

$nZn^{2+} + 2M^{n+}$--Bentonite $\rightarrow$ $2M^{n+} + nZn^{2+}$--Bentonite

**n:** Exchangeable cation valence.

**M:** Exchangeable cation by Bentonite like Na, K, Mg and Ca.

Arias and Sen [4] studies indicate clearly that zinc metallic ion adsorption ($Zn^{2+}$) on kaolin goes through 02 steps: a very fast adsorption of zinc metallic ion at external surface, followed by intra-particle diffusion inside adsorbent. Equilibrium time is 60 minutes.

Madhava Rao and al [18], studied zinc removal by adsorption on activated carbon from Ceiba pentandra capsule (agricultural waste). Obtained kinetics expressed that equilibrium time is 50 min for initial zinc concentration of 50 mg/l and initial pH = 6.

Kouakou and al [22], tested zinc adsorption on commercial activated carbon, presented 20 ml of homogenized industrial water with 0.1g of activated carbon in a beaker of 250ml, applied many hours of stirring time. Equilibrium time found was 01 hr at pH 6 and at 27°C.

Several studies also confirmed activated carbon effectiveness to remove zinc as Monser and Adhoum study [23], who produced steady bed column results on ions adsorption for Cu(II), Zn(II) and Cr(VI) on modified activated carbon with sodium-diethyl-dithiocarbamate (SDDC). They found that activated carbon modified with SDDC has an effective displacement capacity for Cu (II) (04-times), Zn (II) (04-times) and Cr (VI) (02-times) greater than unchanged activated carbon.

They reported also that SDDC is adsorbed on hydrophilic part of carbon surface.

Gräfe and Sparks [24] studied zinc and arsenic kinetics of adsorption on goethite. They found that 95 % and 72 % of zinc and arsenic were adsorbed in first 08hrs at pH 7.

**Effect of adsorbent dose**

The effect of adsorbent dose on the removal of zinc was studied for initial zinc concentration of 5mg/l. Dose of adsorbent was varied from 0.5 to 8 g/l and the solutions where kept under stirring for 20 min, 30 min, 01 hr and 03 hrs in presence of bentonite goethite, PAC and kaolin respectively. For each treated sample, residual zinc content and final pH was measured.

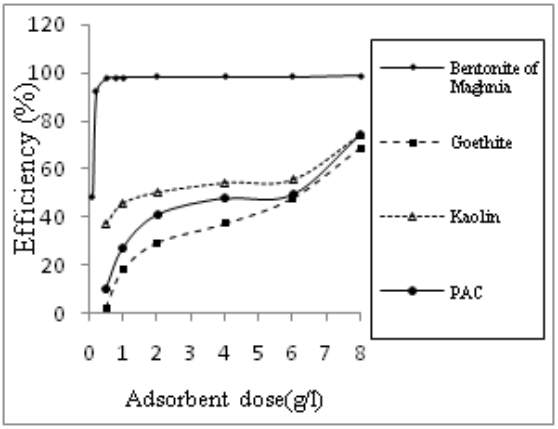


Figure 2: Effect of adsorbents dose on removal of zinc (5 mg/l)

Obtained results show that zinc removal efficiency increases with introduced adsorbent dose increasing (fig 2). At 8g/l of bentonite, efficiency reaches 98.68 % and all residual contents obtained in zinc are largely low than 3 mg/l potability standard [25]. Efficiency stability over bentonite dose of 1g/l is due to adsorption site saturations.

Goethite, Kaolin and PAC efficiencies increase with adsorbent dose increasing and reach 68.68, 74.4 and 74.2%, respectively, for 8g/l dose of each adsorbent.

We have obtained same result by treating distilled synthetic water solution, initially containing 5 mg/l Zinc and varying bentonite dose (Calcic Bentonite) from 0.1 to 8 g/l [14]. According Zhang and al [26], zinc removal efficiency (100 mg/l) increases with Bentonite dose increasing (0.2 to 2 g/l).

Madhava Rao and al [18] studied activated carbon dose (100 to 400 mg/l) effect, they found that efficiency get improved with adsorbent dose increasing until 300 mg/l, almost reaches 100%. Beyond this dose, efficiency remains nearly stable. Same result was found by Depci and al [19],who tested (VAAC) carbon dose effect on Pb (II) and Zn (II) removal, 0.01-0.2 g VAAC was added to test-tubes containing 40 mg/l of ion in solution. Obtained results showed efficiencies of 91.5 % and 78 % for Pb (II) and Zn (II) respectively with 0.1 g VAAC. Above this weight, efficiencies became almost constant.

Mishra and Patel [27] found same result using kaolin (5 to 20 g/l) to treat distilled synthetic solutions initially containing 100 mg/l of zinc.

Table 1 show that pH equilibrium increase as increasing dose of each adsorbent tested.

**Table 1 :** pH evolution according to both adsorbent dose at equilibrium time.

| Adsorbent dose (g/l) | 0.5 | 2 | 4 | 6 | 8 |
|---|---|---|---|---|---|
| Goethite | 5.62 | 5.63 | 5.65 | 5.73 | 5.93 |
| Bentonite | 7.56 | 7.94 | 8.02 | 8.12 | 8.33 |
| Kaolin | 6.19 | 6.20 | 6.22 | 6.26 | 6.46 |
| PAC | 6.02 | 6.22 | 6.62 | 6.69 | 6.65 |

Basta and Tabatabai [28], proposed the following mechanism for metal adsorption on negative bentonite sites:

$$M^{2+} + H_2O \leftrightarrow MOH^{+} + H^{+}$$
$$MOH^{+} + X^{-} \leftrightarrow XMOH$$

**X** : Bentonite surface ; **M** : Metal.

Also, regarding reached pH for increasing bentonite doses, a zinc precipitation phenomenon as hydroxide form, can also be generated [29].

Benjamin and Leckie [30], proposed the following mechanism to describe divalent metal adsorption at iron hydroxide surface :

$$SOH_x + Me^{2+} \Longleftrightarrow SOMe^{(2-x)+} + x\,H^{+}$$

**x:** Proton number free by adsorbed metal (**Me**).

**SOH. :** Average site surface concentration, occupied by metal.

**Effect of initial concentration of zinc**

After using 1 g/l of adsorbent and varying initial ion metal concentration from 2 to 20 mg/l, solutions were stirred during contact time of 20 min, 30 min, 01 hr and 03 hrs contacts with bentonite, goethite, PAC and kaolin respectively.

According to results shown in Fig 3, we can notice that al curves represent same rate. Treatment efficiency decreases with initial zinc increasing

Efficiencies decrease may due to adsorption site saturation at each adsorbent surface.

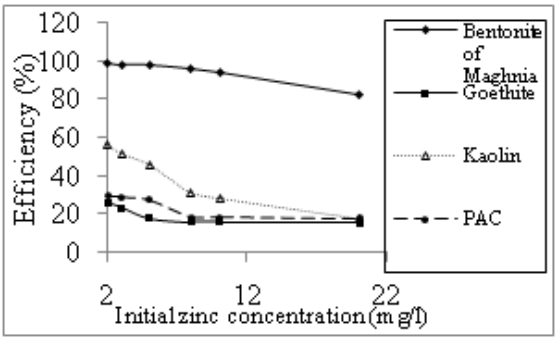


Figure 3: Effect of Initial concentration in removal of zinc

By varying initial zinc content from 2 to 20 mg/l and setting calcic bentonite dose at 1g/l, we also noticed zinc removal efficiency decreasing [14]. Same note was done by Zhang and al, [26], when varying Zn(II) initial content between 30 and 250 mg/l for same bentonite dose.

Shahwan and al [15], results confirmed that kaolin effectiveness in zinc removal is noticeable at low concentrations (1, 100 and 500 mg/l) of this metal. This effectiveness decreases progressively for initial zinc contents from 1 mg/l to 10000 mg/l. They also studied $MgCO_3$ - kaolin mixture to remove zinc. Initial zinc content was varied from 0 to 2500 mg/l and set kaolinite mass with variation in $MgCO_3$ content (5, 10, 25 and 60 %), noticed adsorptive capacity increasing with $MgCO_3$ percentage raising and with initial zinc content raising from 0 to 200 mg/g for 60 % of $MgCO_3$.

Balistrieri and Murray [31] have tested goethite to remove zinc in synthetic solutions which initial zinc contents range from 0.037 to 1.9 mg/l. Results noticed that efficiencies decrease with initial zinc content whatever was pH treatment (5 to 8).

A same result was found by Theis and West [32], for solutions of 0.45 to 4.33 mg Zn/l treated in presence of 0.6 g/l of goethite.

According to Madhava Rao and al [18], efficiencies decrease with initial zinc content increasing from 40 to 200 mg/l at pH 6 and activated carbon fixed dose of 10g/l.

While Depci and al [19], tested the activated carbon (VAAC) prepared with local agricultural waste as apple-plup to remove lead and zinc, found that both metal adsorptive capacity increases when initial concentration increases (25, 30, 35 and 40 mg/l ) at

fixed dose of adsorbant (4 g/l). Same result found by Ramos and al [33], who studied zinc removal on three carbon types ( Carbon from Mexico, Carbon modified with HSL and Carbon modified with F-300 and F-400). Initial zinc content was ranged from 0 to 60 mg/l with 1g/l previous carbons at pH 7.

## Zinc adsorption isotherm

Results operation according to Freundlich and Langmuir laws is made by considering a fixed adsorbent dose (1g / l) and varying concentrations of initial variable Zn concentrations from 2 to 20 mg/l.
Linearized forms o f these models are expressed by Weber and al [34] :
Freundlich isotherm equation:

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log C_e$$

Langmuir isotherm equation:

$$\frac{m}{x} = \frac{1}{q_m} + \frac{1}{q_m \times b} \times \frac{1}{Ce}$$

**Ce** : Zinc concentration at equilibrium (mg/l)

**x = ($C_0$ – Ce)** : Fixed zinc quantity (mg/l)

**m** : Adsorbent mass (g)

**$q_m$** : Ultimate adsorption capacity (mg/g)

**k, n, b** : Adsorption constants

Through least-squares method adjustment, we obtain for each studied law and tested adsorbent, straight with correlation coefficients between 94.9% and 99.3% (Figure 4). Various constants deduced from obtained straight equations are summarized in Table 2.

Linearized forms application of Freundlich and Langmuir laws allowed verifying that these two models are appropriate and zinc removal efficiencies vary in same way with both models. Behavioral differences seem to appear because of maximum adsorption capacity $q_m$ for each adsorbent. Best adsorption capacity is obtained for bentonite 13.89 mg/g, then 3.70., 3.29 and 2.91 mg/g for kaolin, PAC and goethite respectively.

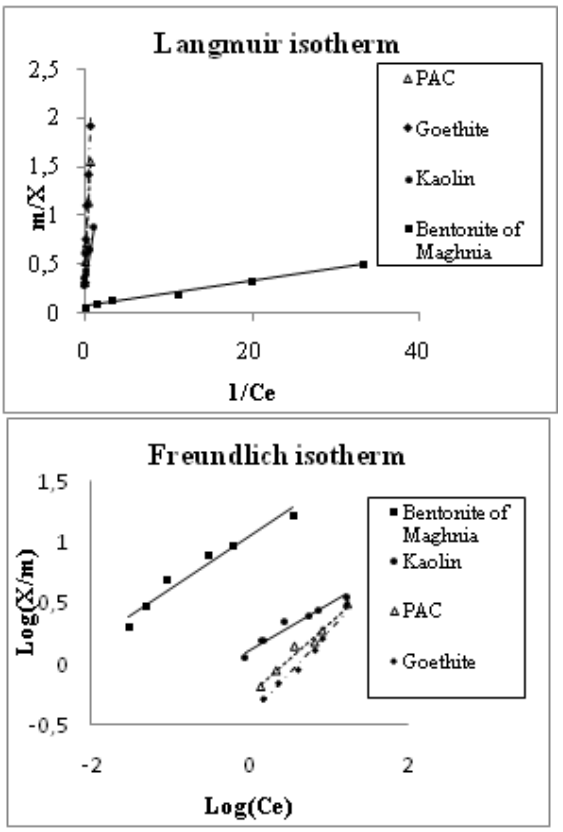


Figure 4: Freundlich and Langmuir isotherms for zinc removal on bentonite of Maghnia, goethite, PAC and kaolin.

Table 2 : Freundlich and Langmuir isotherm parameters.

| Adsorbent | Freundlich | | | Langmuir | | |
|---|---|---|---|---|---|---|
| | n | k | $R^2$ | $q_m$ (mg/g) | b (l/mg) | $R^2$ |
| Bentonite | 2.35 | 11.07 | 0.949 | 13.89 | 5.54 | 0.993 |
| Kaolin | 2,65 | 1,32 | 0.951 | 3,70 | 0.50 | 0.989 |
| Powdered activated carbon | 1,69 | 0,55 | 0,973 | 3 ,29 | 0,18 | 0,978 |
| Goethite | 1,41 | 0,37 | 0.980 | 2,91 | 0.14 | 0.961 |

## Effect of pH

Zinc adsorption experiments were conducted in presence of 1g/l of adsorbent and 5 mg/l of zinc. pH was adjusted to 4, 6, 7and 9 successively and maintained constant during stirring time about 20 min 30 min, 01 hr and 3 hr and 01 hr for bentonite, goethite, kaolin and PAC, respectively, using NaOH (0,1N) and HCl (0,1N) solutions.
Experiments results (Fig 5) shows a gradual increase in adsorption with increase of pH.
For bentonite, kaolin, PAC and goethite, best efficiencies are obtained in basic medium while best one is at pH 9, with removal rates at 98.44%, 82.2%, 85.15% and 92.26 %, respectively.

Adsorption increasing with pH is due to adsorption site number increasing depending on pH (hydroxyl groups, oxydes and clay minerals) as well as $H^+$ ion competition reduction and preferential ($ZnOH^+$) hydrolyzed species adsorption.

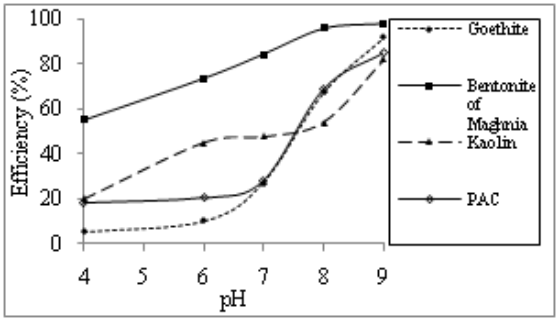


Figure 5 : Effect of pH on removal of zinc (5 mg/l) by adsorption on bentonite, goethite, kaolin and PAC.

Sen and Gomez, Larakeb and al, Mohammed Azizi and al [12, 14, 13], confirmed that zinc removal efficiency increase on bentonite with pH increasing.
According to Abollino and al, Achour and Youcef, Youcef and Achour [28, 35, 36], metallic ions adsorption on sodic bentonite decreases with pH decreasing.
At low pH, hydrogen ions compete with heavy metals for surface sites. In addition, $Si\text{-}O^-$ and $Al\text{-}O^-$ groups are less deprotonated and hardly form complexes with divalent and trivalent ions.
Zhang and al, [26] showed that zinc removal by bentonite as adsorbent depends highly on pH. Removal percentage increases with pH increasing from 1 to 7. Low efficiencies at pH <2 may be due to competition raise for adsorption sites between $H^+$ and $Zn^{2+}$. By pH increasing, negative charge site number increases which facilitates more $Zn^{2+}$ ions adsorption. At pH> 7, $Zn(OH)_2$ precipitation plays the main role in $Zn^{2+}$ removal.
The study of removal of copper, zinc and cadmium by adsorption on goethite enhanced that adsorption zinc efficiency increase from 15 to more than 90 % with pH increasing between 6 and 7 [37].
Arias and Sen [4] and Mishara and Patel [26] applied experiments confirmed that zinc removal efficiency on kaolin increases with pH increasing.
Madhava Rao and al, [18] indicated that best efficiency of removal of zinc by adsorption on carbon is founded at pH 6 for initial 50 mg/l zinc concentration, 300 mg/l carbon dose and 50 min stirring time. Ramos and al,[34] tested pH effect on adsorption phenomenon. They noticed that pH solution raised during Zn (II) adsorption on carbon F-400 and diminish during adsorption on carbon from Mexico. Consequently, both $Zn^{+2}$ and $H^+$ ions were simultaneously adsorbed on carbon F-400 surface and probably competed for same ions. For carbon from Mexico, $Zn^{+2}$ ions were adsorbed while $H^+$ ions were desorbed on its surface. This last phenomenon, known as ions exchange, and $H^+$ was probably adsorbed from surface site where $Zn^{+2}$ can be adsorbed.

The tests of pH effect on copper, zinc and cadmium adsorption on goethite, show that zinc adsorption efficiency increase from 15 to 80% for copper and lead at pH 7 and 8, respectively, 70% at pH 7 for zinc and from 50 to 60% at basic medium (pH 8 and 9) [38].

## Conclusion

Our work aimed to study zinc removal possibilities by adsorption on clays (bentonite of Maghnia, kaolin), on an iron oxide (goethite) and on powdered activated carbon (PAC). Applied study, we achieved, allowed us to notice that:
- Equilibrium time is reached after 20 min of stirring solutions of zinc (5 mg/l) in presence of bentonite of Maghnia and 30 min, 60 min and 180min in presence of goethite, kaolin and powdered activated carbon respectively.
- Zn removal efficiency is improved with adsorbent dose increasing (0.1 à 8 g/l). For bentonite doses greater than 1g/l, zinc removal efficiency exceeds 98.68%. However, at 8g/l dose of kaolin, PAC and goethite, it only reaches 74.4, 74.2 and 68.68%, respectively.
- Zinc removal, by adsorption on above adsorbents, is more effective for water at low zinc contents, and treatment efficiency decreases with initial zinc content increasing (2 to 20 mg/l).
- Zinc adsorption is influenced by pH. Best efficiencies were obtained on basic mediums.
Tested adsorbent efficiency for zinc removal in synthetic solution follows the order:
bentonite of Maghnia > kaolin > PAC > goethite, independently from reaction parameter variations (contact time, adsorbent dose, initial zinc content and pH of treatment).

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