

# Laterite as a Filter Media for Reducing Some Priority Inorganic Contaminants in Water

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## 1. Introduction

Occurrence of elevated concentration of different inorganic pollutants in surface and/or ground water has created immense social problems. Among the various toxicants, heavy metal ions and fluoride are the priority contaminants, considering their magnitude, time of residence and human health hazards. While the heavy metals enter the water bodies primarily through industrial discharge (1), fluoride may come both from industries as well as via geological sources (2). All these toxicants are of serious concerns to the environmentalists due to their non-biodegradable character (3). Occurrence of excessive fluoride in ground water, causes serious and irreversible health damage, known as fluorosis. At present twenty nine countries including India are facing the problem due to excess fluoride in ground water (4). A conservative estimate of fluoride victims around the globe, at present is 67 million while 64 million people are at risk (5).

In many cases the water users in India have completely or partially rejected the source or are compelled to use it with reluctance. Different technologies are available for removing or reducing the excess level of toxicants so that the water quality may be brought to acceptable levels as per the recommendation of WHO (6). These include ion exchange, reverse osmosis, precipitation and adsorption (7). The choice and utility of a particular technique is judged from its simplicity, efficiency and cost effectiveness. Considering the above facts adsorption has several advantages and a wide variety of adsorbents ranging from natural to waste materials, as well as synthetic substances are reported (8÷10).

The present study is intended to use laterite for effective removal of heavy metals viz., copper, nickel, zinc and iron as well as fluoride from water. Laterite is a weathered rock available abundantly in several parts of the country. It is therefore a readily available, low cost material. Moreover the operation process is simple and can be used by rural people also.

## 2. Experimental

All the chemicals were of analytical-reagent grade. Stock solutions (1000 ppm) of Cu(II), Ni(II), Zn(II), Fe(II) were prepared by dissolving the respective metal salts in doubly distilled water. Fluoride solution (stock) of 100 ppm was prepared by dissolving potassium fluoride in doubly distilled water, kept in plastic container. Laterite obtained from Bankura, (West Bengal, India) was washed with doubly distilled water, air-dried and sieved at different size fractions.

### 2.1. Apparatus

Perkin-Elmer atomic absorption spectrophotometer and UV-VIS spectrophotometer were used for determination of metal ions and fluoride respectively. Systronics pH meter was used to measure the pH of the aqueous solutions. In AAS an air-acetylene flame was used with the observation at 10 cm above the burner with the following wavelengths; Cu: 327.4, Ni: 232.0, Fe: 372.0 and Zn: 213.9 nm (11).

### 2.2. Procedure for adsorption experiment

The sorption behaviour of various metals was examined under both static and dynamic conditions. The operational variables were optimized through the static process. The static method was used to determine the capacity of laterite, as well as the kinetics of adsorption process. The dynamic method was used to determine the influence of flow rate and sample volume on the column operation.

*Static process:* 50 ml of solute solution after pH adjustment was equilibrated with 1.0 g of laterite in a batch reactor and shaken till the equilibrium is attained. Solute concentration in the supernatant was measured (11) for the calculation of percent uptake.

*Dynamic process:* The chromatographic column used was a glass tube (30×1.0 cm) with a coarse sintered-glass disc and a tap at the bottom that was prepared by careful filling of laterite, the bed length being about 20 cm. A fixed volume of solute solution was allowed to pass through the column at a flow rate of 5.0 ml/min. A definite volume of effluent was collected at regular interval and the concentration was measured following the standard method.

### 3. Results and Discussion

The physico-chemical composition of laterite was determined following standard method (12) and presented in Table 1. Major components are silica, alumina and iron (III) oxide with minor components of different metal oxides viz. sodium, potassium, calcium, magnesium, manganese and titanium.

**Table 1.** Physico-chemical composition of Laterite

**Tabela 1.** Skład fizyko-chemiczny laterytu

| Constituent                    | Percentage by weight |
|--------------------------------|----------------------|
| SiO <sub>2</sub>               | 67.200               |
| Al <sub>2</sub> O <sub>3</sub> | 9.350                |
| Fe <sub>2</sub> O <sub>3</sub> | 10.000               |
| Na <sub>2</sub> O              | 0.200                |
| K <sub>2</sub> O               | 2.730                |
| CaO                            | 0.030                |
| MgO                            | 1.000                |
| MnO <sub>2</sub>               | 0.052                |
| TiO <sub>2</sub>               | 1.270                |
| Loss on ignition               | 6.100                |

#### 3.1. Optimisation of operational variables in static process

Suitable applications of laterite for the adsorption of solutes demand the process to be both thermodynamically and kinetically favourable. To achieve the maximum efficiency, it is necessary to optimise the operational variables. Equilibrium shaking time, dose, temperature and pH, are the major guiding factors for batch process, while volume of sample solution and flow rate are important for column study.

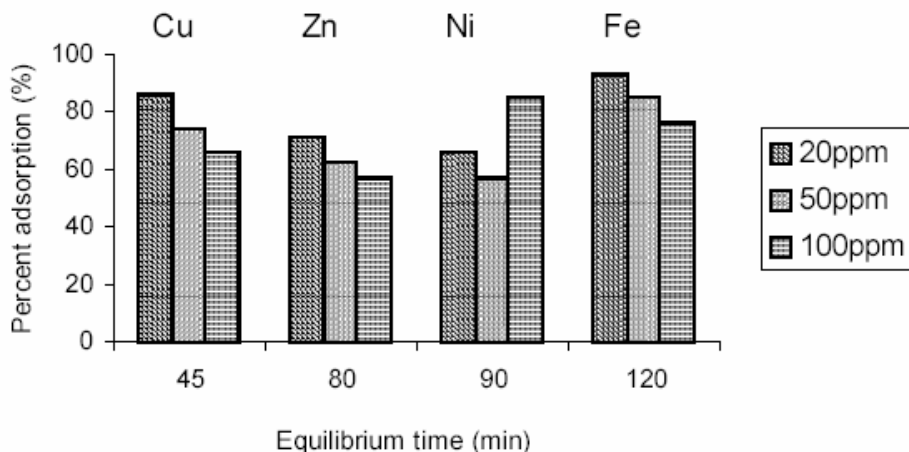
*Adsorption as a function of shaking time:* The time taken for the adsorption of solutes and the attainment of the equilibrium condition is of considerable importance. It is observed that different solutes required different times for attaining equilibrium with different extent of uptake. Within the series of studied metal ions, equilibrium time ( $t_{eq}$ ) for copper ion is shortest. The observed order is found to be: Cu(II)>Zn(II)>Ni(II)>Fe(II). Ferrous ion shows highest uptake of 93% while that for copper, nickel and zinc are 86, 79 and 71% respectively for an initial concentration of 20 ppm (Fig. 1). It is further observed

that as the initial concentration is varied from 100 to 20 ppm, the uptake increases significantly for all the metal ions (Table 2). Adsorption efficiency of laterite was tested for fluoride concentration in the range of 10 to 50 ppm. A maximum uptake of 78.2% (corresponding to 10 ppm) is observed at the equilibrium time of 195 minutes.

**Table 2.** Adsorption characteristics of the solute ions

**Tabela 2.** Charakterystyka adsorpcji jonów z roztworu

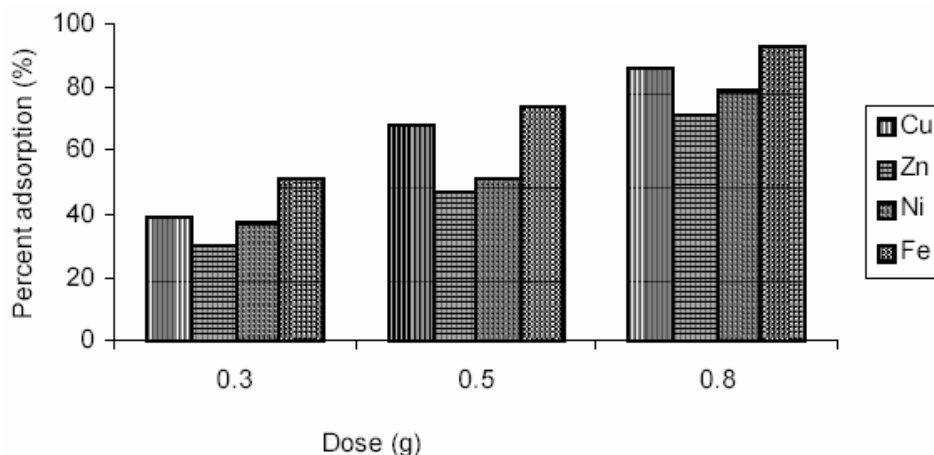
| Solute         | $t_{eq}$ , min | $t_{1/2}$ , min | Uptake at various experimental conditions (%) |                    |                      |                   |
|----------------|----------------|-----------------|---|--------------------|----------------------|-------------------|
|                |                |                 | Dose, g (0.3÷1.0)                             | Size, mm (0.3÷0.8) | Speed, rpm (400÷100) | Temp, K (313÷293) |
| Cu(II)         | 45             | 20              | 39-86   | 86-32              | 86-46                | 91-77             |
| Zn(II)         | 80             | 29              | 30-71   | 70-27              | 70-41                | 79-59             |
| Ni(II)         | 90             | 35              | 37-79   | 78-30              | 78-51                | 85-67             |
| Fe(II)         | 120            | 45              | 51-93   | 93-44              | 93-63                | 98-81             |
| F <sup>-</sup> | 195            | 40              | 21-78.2                                       | 78.2-30            | 78.2-33              | 64-41             |



**Fig. 1.** Influence of initial metal concentration on adsorption

**Rys. 1.** Wpływ początkowego stężenia metalu na adsorpcję

*Adsorption as a function of dose of laterite:* The minimum amount of laterite corresponding to the maximum solute sorption at a definite solute concentration is taken as the optimum dose. Laterite dose was varied from 0.3 to 1.0 g and there is increase in the percent uptake of metal ions (Fig. 2). Highest adsorption was observed for 0.8 g for all the metal ions, while optimum dose for fluoride was found to be 1.0 g. Hence, for all subsequent experiments laterite dose of 1.0 g was maintained.



**Fig. 2.** Influence of dose on adsorption

**Rys. 2.** Wpływ dawki na adsorpcję

*Adsorption as a function of particle size of laterite:* Adsorption of solutes was performed with laterite of different particle sizes, viz. 0.8, 0.5 and 0.3 mm. The increase in the extent of percent adsorption of metal ions with decreased particle size is presented in Fig. 3. Similar behaviour was observed for fluoride also and an increase from 30 to 78.2% was observed.

*Adsorption as a function of agitation speed:* The effect of agitation speed on the solute uptake was studied within the range 100 to 400 rpm, for a definite concentration of solute and pH. The percent uptake increases as the agitation speed is increased. It is possibly due to the different rate of solute-laterite interaction (13). Influence of agitation speed on the uptake of metal ions is presented in Fig. 4.

*Adsorption as a function of temperature:* Temperature is an important parameter in the context of adsorption on solid phase. An increase in the percent adsorption was observed corresponding to the increase in temperature from 293 to 313 K. For fluoride (50 ppm) the increase was found from 41 to 64%. Adsorption behaviour of different metal ions is presented in Fig. 5.

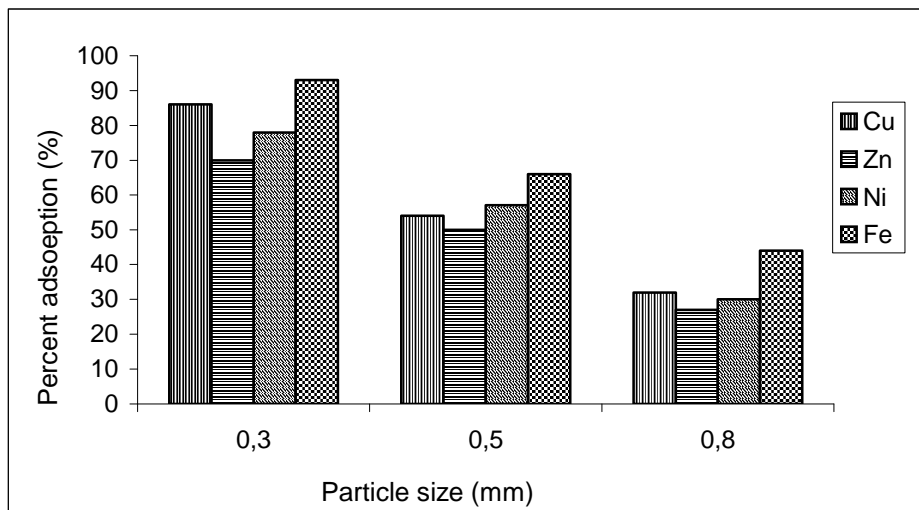


Fig. 3. Influence of particle size on adsorption

Rys. 3. Wpływ rozmiaru cząsteczki na adsorpcję

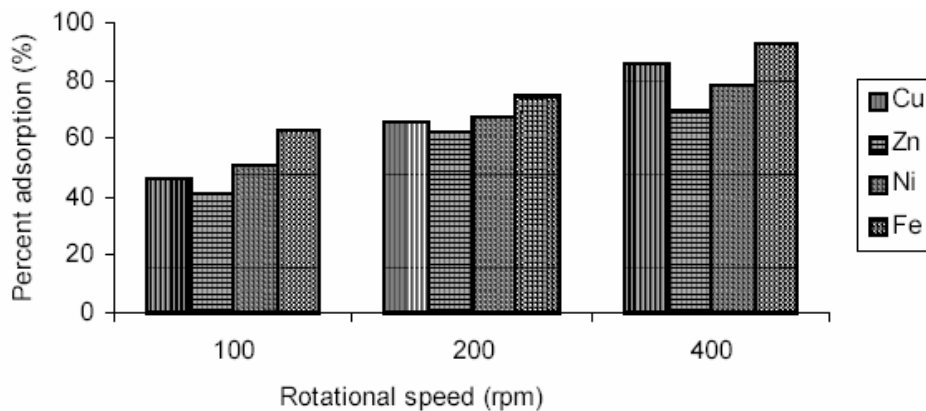
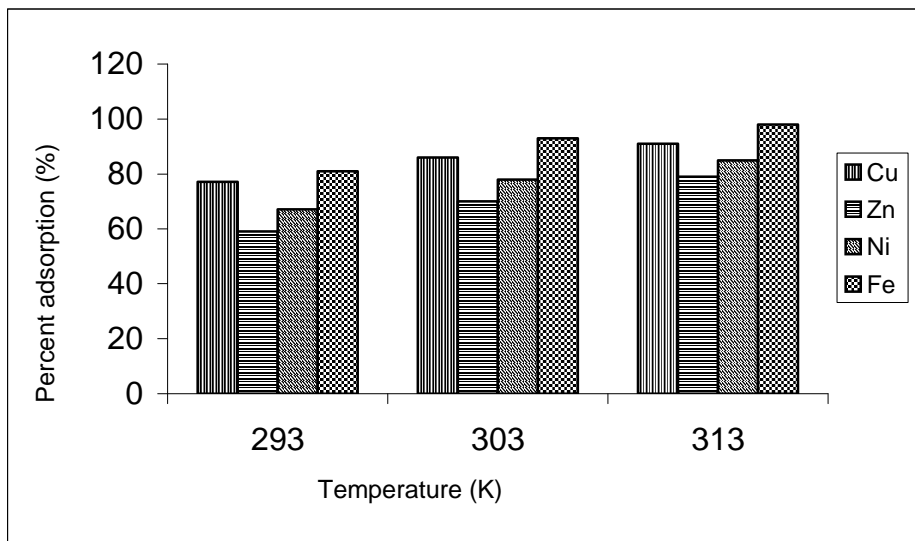


Fig. 4. Influence of rotational speed on adsorption

Rys. 4. Wpływ prędkości obrotowej na adsorpcję



**Fig. 5.** Influence of temperature on adsorption

**Rys. 5.** Wpływ temperatury na adsorpcję

*Adsorption as a function of pH:* Adsorption of solute on a solid surface is known to be dependent on the pH of the solution as the surface charge, characterized by pHZPC of an adsorbent vary with pH. It is expected that at  $\text{pH} > \text{pHZPC}$  the negative charge density on laterite surface increases, leading to increased adsorption of cationic solute and decreased adsorption of anionic solute. Simultaneously the pH dependent speciation of solutes play important role (14). In order to avoid the hydrolysis of metal ions and complexity in speciation all the experiment were performed in the pH 6.8. However the detailed study on the mechanism of pH dependent adsorption on laterite will be taken up in future communication.

### 3.2. Adsorption equilibrium and adsorption isotherm

The ability of laterite to extract solutes from aqueous solution was evaluated by measuring adsorption isotherm, correlating the equilibrium adsorption amount on laterite and equilibrium concentration in solution. The L-type adsorption behaviour, predicted from the equilibrium data in the present system suggests favourable adsorption and also a strong tendency of monolayer formation (13).

### 3.3. Optimisation of the column operation

Solute solution (1000 ml) at optimum pH was passed through the filter column loaded with the laterite in a down flow manner. The flow rate was varied between 1.0 to 10.0 ml/min and there was no significant difference due to change in flow rate. It is found the removal efficiency of different metal ions follow the order: Fe(II) > Cu(II) > Ni(II) > Zn(II). Fluoride removal efficiency was more than 96% during column operation.

### 3.4. Kinetic feasibility of the process:

From the equilibrium data, the loading half time ( $t_{1/2}$ ), the time required to reach 50% sorption of the total capacity was calculated. It is found that while  $t_{1/2}$  value lies between 20 to 45 minutes for the metal ions (Table 2), it is 40 minutes for the fluoride adsorption. The lower value of  $t_{1/2}$  indicates that the kinetics of solute-laterite interaction is sufficiently rapid (13).

### 3.5. Mechanism of solute-laterite interaction

Laterite is primarily composed of silica, alumina and iron (III) oxides (Table 1). When it is soaked in water for several hours the oxides get converted to oxohydroxides of silica, aluminium and iron. The Si-O and Al-O bonds are much stronger than Fe-O bonds. The governing interaction for metal ion-laterite is expected to be of ion exchange type (probably through replacement of weak Fe (III) sites). The fluoride-laterite interaction can be explained from the fact that ionic radius (15) of fluoride ion (1.40 Å) and hydroxyl ion (1.36 Å) are similar and these could be easily exchangeable effecting fluoride adsorption on metal hydroxides.

### 3.6. Cost viability of the laterite filter media and conclusion

Activated carbon is considered as a universal and most efficient adsorbent for treatment of water contaminated by a wide range of pollutants (16). But its higher cost limits its use. Therefore, more research is directed towards the search of alternative adsorbents. In India laterite is readily available in plenty, as a large area is covered by laterite. Therefore laterite filter media can be used as an alternative, for some metal ions and fluoride removal. Moreover the capacity of laterite filter media in suitable experimental conditions is more or less comparable to activated carbon, at least for some solutes. Further the laterite media can be extended for development of a simple household filter.



## References

1. **Sarkar M., Dutta P.K.:** *Sorption Recovery of Copper Ion in Aqueous Solution* Jr. Indust. Poll. Control, 17, 179–190. 2001.
2. **Sarkar M., Chakrabarty S., Banerjee A.:** *Fluoride Contamination in Groundwater in Birbhum District of West Bengal – A Geoenvironmental Hazard* Ed. A. G. Paithankar, P. K. Jha, R. K. Agarwal, Oxford IBH Publishing Co. Pvt. Ltd., New Delhi 2000. p.191–194.
3. **Horwarth D. J.:** *The Substances and Health – A Handbook* Marcel Dekker Inc., New York 1996.
4. *Fluoride Research and Rural Development Foundation Report* Ministry of Rural Developments, Government of India. 1999.
5. **Sarkar M.:** *Occurrence of High Fluoride in Ground Water of Birbhum District of West Bengal* Proc. 5th All Poland Conf. 2001.
6. *WHO Guidelines for Drinking Water Quality* Vol. I: World Health Organisation, Geneva 1984.
7. **Gupta V.K.:** *Equilibrium Uptake, Sorption Dynamics, Process Development and Column Operations for Removal of Copper and Nickel from Aqueous Solution and Waste Water Using Activated Slag, A Low Cost Adsorbent* Ind. Eng. Chem. Res., 37, 192–202. 1998.
8. **Jeon B.H., Dempseis B.A., Burgos D., Royer R.A.:** *Sorption Kinetics of Fe(II), Zn(II), Co(II), Ni(II), Cd(II) and Fe(IV) / Me(II) onto Hematite* Wat. Res., 37, 4135–4142. 2002.
9. **Sarkar M., Dutta P.K., Das M.:** *Solid Phase Extraction for Decontamination of Alkali Metal, Alkaline Earth Metal and Ammonium Salts from Heavy Metal Ions* J. Colloid Interface Sc., 246, 263–269. 2002.
10. **Sarkar M., Dutta P.K.:** *Equilibrium Studies on the Optimization of Solid Phase Extraction Using Modified Silica Gel for Removal, Recovery and Preconcentration Prior to Determination of Some Metal Ions from Aqueous Samples of Different Origin* Ind. Eng. Chem. Res., 41(26), 6745–6750. 2003.
11. APHA, AWWA, WPCF: *Standard Methods for Examination of Water and Wastewater* 19th ed.: APHA, Washington 1999.
12. *Method of Soil Analysis* Pt I & II: Ed. C. A. Black; Am. Soc. Argon., Madison 1965.
13. **Sarkar M., Dutta P.K.:** *Sorption Aided Process for Removal and Recovery of Zinc(II) Using Salicylaldoxime Immobilized Silica Gel* Ind. J. Chem. Tech., 9, 245–250. 2002.
14. **Sarkar M., Banerjee A., Pramanick P.P.:** *Defluoridation of Fluoride Rich Drinking Water – an Ecotechnological Approach* Proc. National Symposium on Recent Advances In The Methods Of Chemical Analysis In Industry And Environment, 2003.
15. **Cotton F.A., Wilkinson G., Gaus P.:** *Basic Inorganic Chemistry*, John Wiley & Sons. N.Y. 1976.
16. **Swamy M.M., Mall J.D., Prasad B., Mishra J.M.:** *Removal of Phenol by Adsorption on Coal Fly Ash and Activated Carbon* Poll. Res., 16, 170–175. 1997.

## Lateryt jako medium filtracyjne do usuwania niektórych priorytetowych nieorganicznych zanieczyszczeń z wody

### Streszczenie

Pojawienie się podwyższonych stężeń różnych nieorganicznych zanieczyszczeń w wodach powierzchniowych i/lub gruntowych spowodowało pojawienie się ogromnych problemów społecznych. Spośród wielu różnych substancji toksycznych, metale jony metali ciężkich oraz fluor są zanieczyszczeniami priorytetowymi, biorąc pod uwagę ich rozpowszechnienie, czas pozostawania w środowisku oraz zagrożenie jakie niosą dla życia i zdrowia ludzkiego. Podczas gdy metale ciężkie trafiają do środowiska głównie poprzez zrzut ścieków przemysłowych, to fluor może pochodzić zarówno ze źródeł przemysłowych jak również ze źródeł geologicznych. Wszystkie te związki stanowią bardzo poważny problem z powodu ich trudno biodegradowalnego charakteru.

W badaniach, których wyniki przedstawiono w niniejszym referacie, zastosowano lateryt do efektywnego usuwania metali ciężkich: miedzi, niklu, cynku i żelaza oraz fluoru z wody. Lateryt jest zwietrzałą skałą dostępną w dużych ilościach w wielu częściach Indii. Jest to więc materiał łatwo dostępny i tani. Co więcej proces adsorpcji jest prosty w prowadzeniu i może być stosowany nawet przez ludzi mieszkających na wsi. Główne składniki laterytu to: krzemionka, tlenek glinu, oraz tlenek żelazowy. Pozostałe składniki to różne tlenki metali: sodu, potasu, wapnia, magnezu manganu i tytanu.

Proces sorpcji wybranych metali na laterycie badano zarówno w warunkach statycznych jak i dynamicznych. Metoda statyczna służyła do określenia pojemności sorpcyjnej oraz kinetykę procesu adsorpcji. Metodę dynamiczną zastosowano do określenia wpływu prędkości przepływu i objętości próbki na wyniki adsorpcji w kolumnie.

Badania wykazały, że usuwanie poszczególnych metali zachodziło według następującego szeregu powinowactwa:  $\text{Fe(II)} > \text{Cu(II)} > \text{Ni(II)} > \text{Zn(II)}$ . Efektywność usuwania fluoru w czasie adsorpcji w kolumnie przekraczała 96%.

Na podstawie danych równowagi obliczono czas połowicznego wyczerpania złoża, czyli czas potrzebny na wyczerpanie połowy całkowitej pojemności sorpcyjnej laterytu. Z badań wynika, że wartość ta waha się od 20 do 45 minut dla jonów poszczególnych metali (tabela 2), oraz wynosi 40 minut podczas adsorpcji fluoru. Niższe wartości  $t_{1/2}$  wskazują, że kinetyka interakcji pomiędzy laterytem a usuwanym składnikiem jest wystarczająco szybka.

Wyniki badań pokazują, że pojemność sorpcyjna laterytu jako medium filtracyjnego, w odpowiednich doświadczalnych warunkach jest mniej więcej porównywalna z pojemnością węgla aktywnego, przynajmniej dla niektórych usuwanych substancji. W związku z tym celowe są dalsze badania nad zastępowaniem węgla aktywnego laterytem w prostych domowych filtrach oczyszczających wodę.