

Defluoridation of Potable Water Using Chemically Pretreated Tea Leave Waste through Agitated Non-Flow Batch Adsorption Process

¹Sarfraz Ahmad Khan and ²Nusrat Ali

¹Assistant Professor ²Assistant Professor

Department of Civil Engineering

Sagar Institute of Technology and Management, Barabanki-225001, Uttar Pradesh, India

Abstract: The present study aims to assess feasibility of tea leaf waste as potential adsorbent for defluoridation of potable water. The present work involves batch adsorption technique using SPANDS method to infer optimal values of different adsorption parameters such as adsorbent dose, pH, contact time, stirring rate and adsorbate dose for acid and alkali treated tea leave waste. The optimum sorbent dose was found to be 2.0 g/250 mL, equilibrium was achieved in 90 minutes at 120 rpm and enhanced adsorption was obtained at pH 2 for both acid and alkali treated tea waste. Maximum fluoride removal was observed to be 84.8% for acid treated tea waste and 66.8% for alkali treated tea waste at optimum conditions.

Keywords – Defluoridation, SPANDS, Sorbent, Alkali treated tea waste, Acid treated tea waste, Fluoride removal.

I. INTRODUCTION

Fluorine is one of the elements essential for humans. Fluoride exists in the environment through both natural and anthropogenic sources. However, high concentrations of fluoride have adverse effects for human health and higher animals. Drinking water standards for fluoride according to World Health Organization is 1.5 mg/L as the maximum concentration. In India, 25 million people in 19 states and union territories have already been affected and another 66 million are at risk, including 6 million children below the age of 14 years [Sangam, 2003]¹. In some parts of India, the fluoride levels are below 0.5mg/l, while in other places, fluoride levels are as high as 35 mg/l [Handa, 1975]². Fluoride is widely distributed in geological environment [Abe *et al.* 2004]³ and generally released into groundwater by the slow dissolution of fluorine-containing rocks. Rural population satisfies their water needs from dug wells, deep wells, reservoirs and rivers making these people susceptible to fluoride exposure.

High intake of fluoride through potable water causes dental and skeletal fluorosis. Dental fluorosis, characterized by discolored, blackened, and mottled teeth. Excess fluoride intake also interferes with normal bone development. The early stage of skeletal fluorosis, is characterized by joint pain, sensations of burning, pricking, and tingling in the limbs, muscle weakness, chronic fatigue, and reduced appetite. In the more advanced stages, pains in the bones become constant and some of the ligaments begin to calcify. Abnormal crystalline structure of the bones becomes apparent, and bony spurs begin to appear in joint areas. In the most advanced stage, the extremities become weak and moving the joints is difficult. The vertebrae partially fuse together, crippling the patient.

CONCENTRATION OF FLUORIDE IN DRINKING WATER AND ITS EFFECTS ON HUMAN HEALTH

Fluoride concentration (mg/l)	Effect
nil	limited growth and fertility
< 0.5	dental caries
0.5 - 1.5	promotes dental health, prevents tooth decay
1.5 - 4.0	dental fluorosis (mottling and pitting of teeth)
4.0 - 10.0	dental fluorosis, skeletal fluorosis (pain in neck bones and back)
> 10.00	crippling fluorosis

Source: International Drinking Water Standards, WHO, Geneva

Some defluoridation techniques developed to control fluoride content in water are precipitation method, activated alumina process and ion exchange process; however, due to high cost or lower efficiency or non-applicability on mass scale these techniques are not much in use. The Nalgonda Technique fitted in with this goal, in providing an apparently simple solution to improving water quality. However, it did not achieve the success anticipated, due to its intensive operation requirements. Most of the systems installed became inoperative, as the communities lacked a sense of ownership in the schemes [Daw, 2004]⁴. Adsorption methods are relatively simple, economical, and appropriate for drinking water treatment, especially for small communities. There are many adsorbent that has already

been used by different researchers like sunflower plant dry powder, brick powder, holly oke, peepal leaf powder, activated cotton jute carbon, bagasse ash, burnt bone powder, phosphate-treated saw dust, bone char, etc.

The present paper explores the suitability of chemically pretreated tea leaf waste as potential low cost adsorptive source for defluoridation of drinking water.

II. MATERIALS AND METHODS-

All the reagents used for the present study were of AR grade from E. Merck Ltd. India. The stock solution of 100 mg/L fluoride was prepared by dissolving 221 mg anhydrous NaF in 1 litre of distilled water. This 1 mL of solution has 0.1 mg of fluoride. Fluoride standard solution was prepared by diluting 100 mL stock solution to 1000 mL distilled water. A calibration curve was prepared using standard solutions.

Used tea leaf collected from local college canteen, house, and tea shop etc. was cleaned with warm water to remove sugar and milk sticking on the surface of used tea leaves. The washed tea leaves were sun dried to remove moisture. The powder finally sieved with help of sieve shaker to get particle sizes of 0.5mm-0.2mm to increase the surface area. Adsorbents sample (40 gm) and 400 ml of 1N HNO₃ (nitric acid) have been taken in a 1000-ml conical flask. The mixture gently heated on burner for 20 min after boiling starts. Treated adsorbent washed with distilled water. Washing has been done until maximum color was removed and clear water obtained. Then they were kept in a hot air oven to remove the moisture. This was designated as used acid treated tea leaves.

Leaf biomass powder sample (40 gm) and 400 ml 0.5 N NaOH were taken in 1000-ml conical flask. Then mixture was gently heated on burner for 20 min after boiling started. Using distilled water, the treated biomass was washed and washing is continued until maximum color was removed and clear water obtained. This was designated as used alkali treated tea leaves.

Batch adsorption studies were conducted using Jar test apparatus (Scientific Corporation, India) equipped with stirring paddles with provisions for controlled mixing speed. A spectrophotometer (Systronics, portable) Model -169 was used to analyze fluoride content of water at a wavelength of 570 nm.

Measured volumes (1000 mL) of test samples were mixed using the Jar test apparatus in 1000 mL borosil beakers. After the addition of adsorbent in each beaker simultaneously, the content was mixed at 30 rpm for 60 min. At the end of the stirring period, the beakers were removed slowly from the jar tester platform and the contents of the beakers were allowed to settle for 2 minutes. After settlement of adsorbent, the supernatants were carefully decanted, filtered through Whatman 42 No. filter paper and analyzed for residual fluoride by SPADNS method using SPADNS solution and zirconyl acid reagent as per the procedure of Standard Methods for Examination of Water and Wastewater.

Batch adsorption experiments was conducted to investigate the effect of various parameters like adsorbent dose, pH, stirring rate, initial concentration of fluoride and contact time in 250 mL conical flask.

STANDARD CURVE AT 570 nm

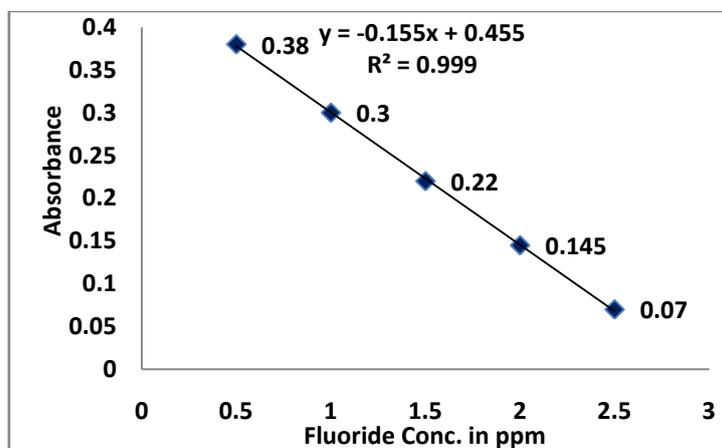


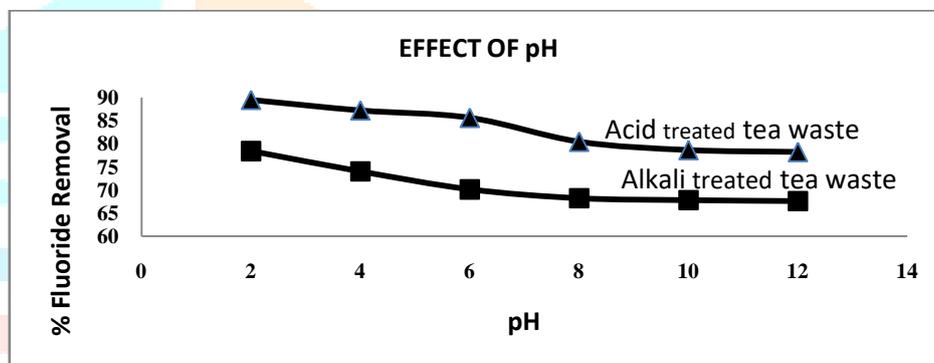
Fig. 1

III. RESULTS AND DISCUSSION-

There are several parameters (adsorbent dose, contact time, initial fluoride concentration, pH, temperature) influencing the fluoride removal efficiency of adsorbent. It is not possible to investigate all of them together within limited resources. Therefore, prior to start actual experimentation, several experiments have been performed in different condition. On the basis the experience gained thereby, some of the most important parameters have been included in present study. Experimental work has been planned to vary one parameter (with in a limited range) at a time keeping rest of input parameters initially same in all the experimental runs to investigate the effect of variation of particular parameter. Batch adsorption studies have been done at different initial concentration of fluoride, contact time and adsorbent dose for tea leaf waste to determine the percentage removal of fluoride from water. The removal of fluoride ions has been studied at a room temperature (29 ± 0.5 °C).

Effect of pH-

The pH of the aqueous solution is a controlling factor in the adsorption process. Thus, the role of hydrogen ion concentration was examined at pH values between 1-8 for both acid treated and alkali treated tea waste. This was adjusted by adding 0.1N HCL or 0.1N NaOH with 50 ml of standard solution of 5 mg/l of fluoride for a contact time of 70 mints with a dose of 8g/l of treated bioadsorbent. The effect of pH on sorption is indicated in Fig 2 .From the result it is observed that there decrease in the extent of removal of fluoride ions with increase in the pH of the solution in both acid and alkali treated tea waste adsorbents. This trend of result may be due to neutralization of the negative charges at the surface of the treated biosorbents by greater hydrogen ion concentration at lower pH values. Similar trends were reported in earlier studies [Bhargava and Killedar, 1991]⁵.

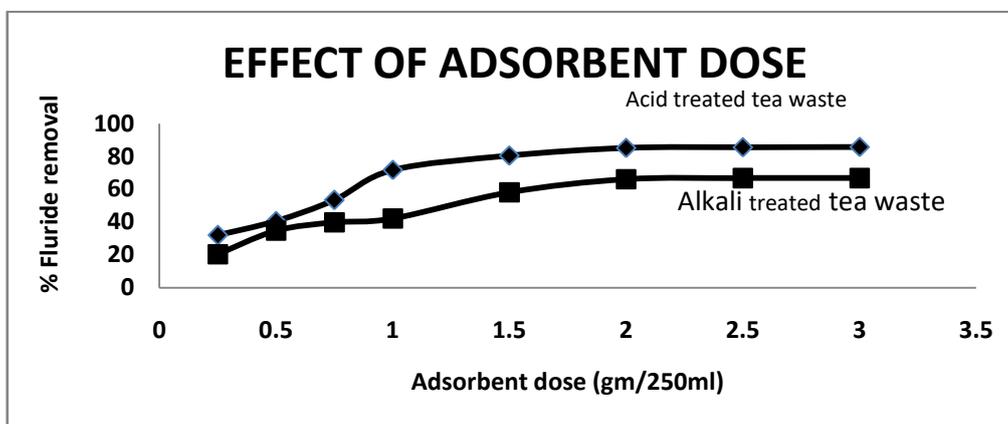


Comparative graph showing effect of pH on the fluoride removal for acid and alkali treated tea waste (Initial fluoride =5 mg/l, adsorbent dose=8 g/l, and contact time=70 min)

Fig. 2

Effect of Adsorbent dose-

The percentage removal of fluoride from water samples having different dose of adsorbent varied in the range 32% to 85.8% for acid treated tea waste and 20.5% to 66.8% for alkali treated tea waste. Results show that the percentage removal of fluoride from water samples increases as concentration of adsorbent increases. It has also been observed that the increase in fluoride removal efficiency after equilibrium point is very less. The response of adsorbent dose on the removal of fluoride is presented in Fig.3. The observations reveal that an increase in the adsorption occurs with the corresponding increase in the amount of adsorbent. The increase in the removal efficiency with simultaneous increase in adsorbent dose is due to the increase in surface area, and hence more active sites were available for the adsorption of fluoride. It can be seen from Fig.3 that after optimum dosage, there is no significant change in percentage removal of fluoride. It is due to the overlapping of active sites at higher dosage, thus, reducing the net surface area. Similar results have been reported by several other investigators [Pandey *et al.*2012, Mahramanlioglu *et al.*2002, Rani *et al.*2012]^{6, 7, 8}.

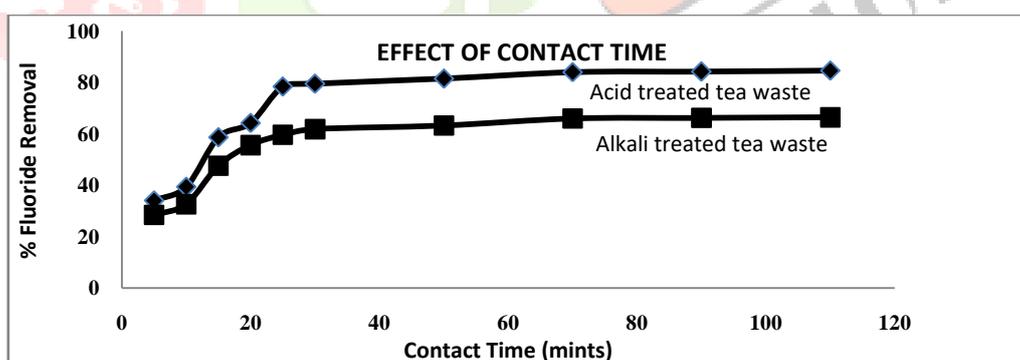


Comparative graph showing effect of adsorbent dose on the fluoride removal for acid and alkali treated tea waste (Initial fluoride =5mg/l, contact time=70 min, and stirring rate= 100rpm)

Fig.3

Effect of Contact time-

Studies on the effect of contact time have been conducted by varying it from 5 to 110 minutes, keeping adsorbent dose of 8 g/l, stirring rate of 100 rpm and initial fluoride concentration taken 5mg/l. Fig.4 shows the progression of adsorption reaction and the percentage removal of fluoride for different contact times. For acid treated tea waste removal efficiency increase up to 70 minute after that there is only slight increase and fluoride is removal almost constant, so the equilibrium time for acid tea waste is found to be 70 minute and the same result 70 min is also reported for alkali treated tea waste adsorbent. The Fig.4 also indicates that the removal of fluoride ions increases with increase in contact time, but after some time, it gradually approaches a constant value, denoting attainment of equilibrium. Further increase in contact time does not increase uptake due to deposition of fluoride ions on the available lead sorption sites on adsorbent material. Decreased extent of adsorption, particularly towards the end of experiment, indicates the possible monolayer of fluoride ions on the outer surface, pores of the adsorbent and pore diffusion onto inner surface of adsorbent particles through the film due to continuous mixing maintained during the experiment [Kabbashi *et al.*2009]⁹.



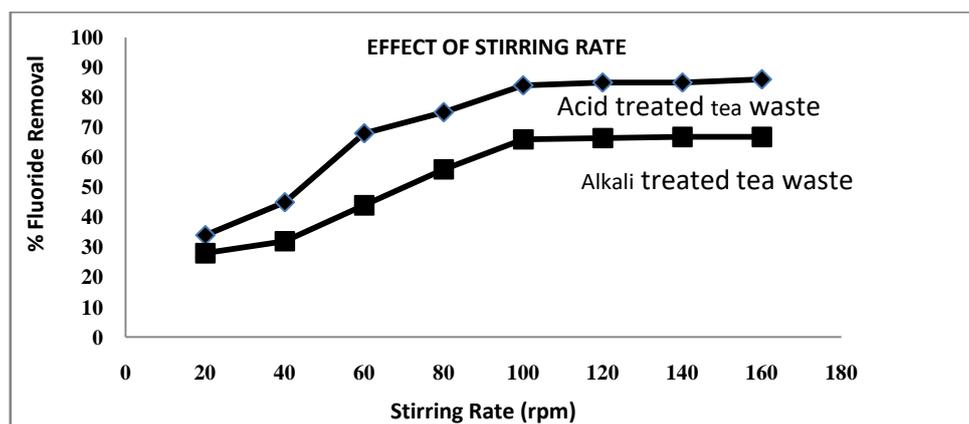
Comparative graph showing effect of contact time on the fluoride removal for acid and alkali treated tea waste (Initial fluoride =5 mg/l, adsorbent dose=8 g/l, and stirring rate= 100 rpm)

Fig.4

Effect of Stirring rate-

Studies on the effect of stirring rate were conducted by varying speeds from 20 to 160 rpm at optimum pH and adsorbent dose of 8 gm/l and contact time of 120 mints. Fig 5 indicates that at a given time, fluoride removal increases with the increase in the speed of agitation in both acid and alkali treated tea waste adsorbents. The reason for the increase is the diffusion of adsorbate towards the adsorbent surface [Kabbashi *et al.*2009]⁹ and also better contact between the adsorbent and adsorbate is possible [Tembhurkar and Dongre, 2006]¹⁰. Similar findings for

fluoride removal by using activated charcoal have been reported by other investigator [Tembhurkar and Dongre, 2006]¹⁰.

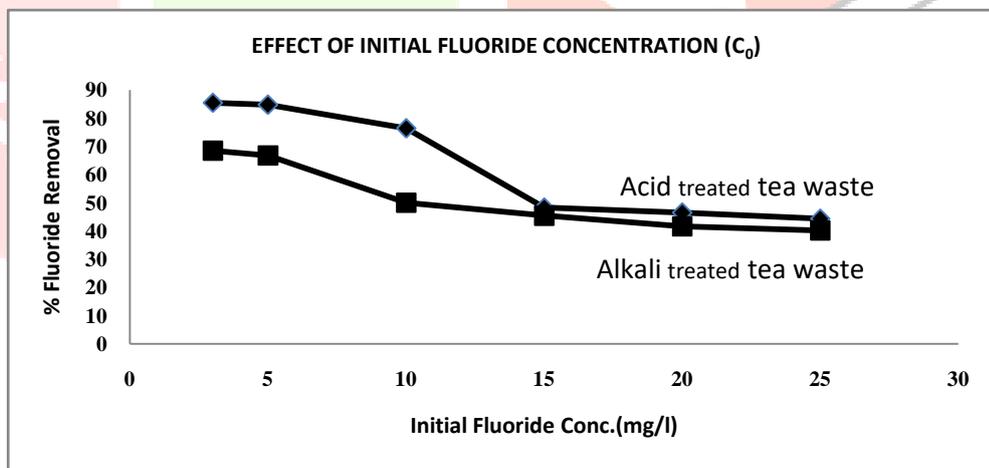


Comparative graph showing Effect of Stirring Rate (rpm) on the fluoride removal for acid and alkali treated tea waste (Initial fluoride =5 mg/l, adsorbent dose=8 g/l, and contact time =70 mints)

Fig.5

Effect of initial fluoride concentration-

Studies on the effect of initial fluoride concentration has been conducted by varying it from 3 to 25 mg/l keeping adsorbent dose of 8g/l, stirring rate of 100 rpm and contact time of 70 minutes. Fig.6 indicates that the percentage removal of fluoride ion decreases with increase in initial fluoride ion concentration in both the case of acid treated and alkali treated tea waste. The percentage removal of fluoride has been observed to be 85.5% at 3mg/L and 44.4% at 25 mg/L for acid treated tea waste. The alkali treated tea waste shows 68.5%, 40.2 % removal at 3mg/l, 25mg/l respectively and it may be because at higher adsorbate concentration, the binding capacity of the adsorbent approaches saturation, resulting in a decrease in overall percent removal. Similar trend of removal has been obtained for treated leave adsorbents [Jamode *et al.* 2004]¹¹.



Comparative graph showing Fluoride removed at equilibrium time for different initial fluoride concentration for acid and alkali treated tea waste (Contact time=70mints, adsorbent dose=8 g/l, and stirring rate= 100 rpm)

Fig. 6

IV. CONCLUSION-

A new medium, waste tea leaves has been developed for fluoride removal in this study. The tea leave waste demonstrated a good capacity of fluoride biosorption, highlighting its potential for the drinking water treatment process. Following points are drawn from above study.

1. The efficiency of acid treated tea waste and alkali treated tea waste as adsorbents for removal of fluoride from water using batch process has been recognized fruitfully.

2. In the first and most important phase, batch study was carried out. In this phase, the removal efficiency of adsorbent used was checked for four varying parameters, viz. adsorbent dose, pH, contact time, stirring rate and initial adsorbate concentration, to find the optimum conditions or equilibrium data.
3. For the effect of adsorbent dose the equilibrium was attained for 8gm/l for both acid and alkali treated tea waste keeping all other parameters constant.
4. For the effect of pH maximum removal efficiency was obtained at lower pH value 2 for both acid and alkali treated tea waste. Keeping in view constrains of post treatment all the other parameters were studied at pH value of 7 ± 0.5 .
5. For the effect of contact time, equilibrium was attained for 70 minutes for both acid and alkali treated tea waste. For the effect of stirring rate, equilibrium was attained for 100 rpm for both acid and alkali treated tea waste.
6. The acid treated tea waste has better removal efficiency than alkali treated tea waste. In case of acid treated, the results were due to neutralization of the negative charge at treated tea waste bioadsorbents surface by greater hydrogen ion concentration, thus reducing hindrance to diffusion of the negatively charged fluoride ions on to the increased active surface of acid treated tea waste bioadsorbents. In case of alkali treated tea waste bioadsorbents it was due to increase of hydroxyl ion concentration in the solution, hence the rate of fluoride ion sorption was maximum on the active surface, due to cation ion exchange phenomenon of alkali treated tea waste bioadsorbents at optimal pH value of 7 ± 0.5 .

V. ACKNOWLEDGMENTS-

I am extremely grateful to Prof. Aqeel Ahmad, Head, Department of Civil Engineering, Integral University, Lucknow, for placing me under the able supervision of Assistant Professor Nusrat Ali for successful completion of my project work. I extend my deep sense of gratitude and indebtedness to my guide, Assistant Professor, Nusrat Ali, Department of Civil Engineering, Integral University, Lucknow, for his kind attitude, keen interest, immense help, inspiration and encouragement which helped me carrying out the research work. It is a great pleasure for me to acknowledge and express my gratitude to the whole teaching and non-teaching staff of Sagar Institute of Technology and Management, Barabanki and Integral University, Lucknow for their understanding, unstinted support and endless encouragement throughout my project work.

References-

1. Sangam, Newsletters of UN inter agency-working group on, Water and Environmental Sanitation in India, (2003) 1-2
2. Handa B K, Geochemistry and genesis of fluoride-containing ground waters in India, Vol.13, No.3, (1975) 275-281
3. Abe I, Iwasaki S, Tokimoto T, Kawasaki T, Nakamura and Tanada S, Adsorption of fluoride ions onto carbonaceous materials, J. Colloid Interface Science 275(2004) 35-39
4. Daw R K, Experiences with domestic defluoridation in India, in: Proceedings of the 30th WEDC International Conference on People-Centered Approaches to Water and Environmental Sanitation, (2004) Vientiane, Lao PDR: 467- 473
5. Bhargava D S and. Killedar D J, Batch Studies of Water Defluoridation Using Fishbone Charcoal, J. Water Pollution Control Federation, (1991) 63(6), 848-858
6. Pandey P K, Pandey M and Sharma R, Difluoridation of water by a Biomass : *Tinospora Cardifolia*, J. Environmental Protection (2012), 3, 610-616
7. Mahramanlioglu M, Kizilcikli I and Bicer I, Adsorption of fluoride from aqueous solution by acid treated spent bleaching earth, J. Fluorine Chemistry (2002); 115(1):41-7
8. Rani B, Maheshwari R, Chauhan AK, Bhaskar NS, Defluoridation of contaminated water employing brick powder as an adsorbent, International J. Science and Nature (2012); 3(1):78-82

9. Kabbashi N A, Abdurahman N H, Muyibi S A and Qudsieh I Y, Development of a Wastewater Treatment System for Chromium Removal Using Chitosan, International J. Chemical Technology, (2009), 1(2), 44-51
10. Tembhurkar A R and Dongre S, Studies on Fluoride Removal Using Adsorption Process, J. Environ Science and Engineering, (2006), 48(3), 151-156
11. Jamode A. V., Sapkal V. S. And Jamode V. S. “Defluoridation Of Water Using Inexpensive Adsorbents” J. Indian Institute of Science, Sept.–Oct. (2004), 84, 163–171

