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Removal of Some Heavy Metal Ions from an Aqueous Systems as Mn(II) and Fe(III) Using Low Cost Products

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Magdy Mohammed Abo zead : Formal analysis; Software; Validation; Visualization; Writing-original draft; Writing-review & editing. Mohamed Saeed El-Attar: Formal analysis; Investigation; Methodology. Sadeek Atia Sadeek: Supervision; Validation; Visualization; Writing-review & editing. Said AbdElazez Shama: Conceptualization; Data curation; Software; Validation; Visualization.

ABSTRACT

The adsorption technique for the process of extracting or separating heavy metal contaminants from solutions was more effective. Activated carbon produced from watermelon rind (**ACWR**), Borokly clay (**BoC**) and Aswany clay (**AsC**) were identified by FT-IR spectroscopy, electron microscope (SEM) and X-ray fluorescence which used to separate Manganese(II) and iron(III) from an aqueous systems. pH, sorbent weights, contact time, temperature and initial concentration of Manganese(II) $\&$ iron(III) were studied to obtain the most favorable conditions for removment of these ions. The results were clear that the removal of metal ions raised with increasing of contact time and sorbent weights. Also, the removal percentage decreased as the initial concentration of the two metals increased. The overall adsorption capacities of **ACWR**, **BoC** and **AsC** for Manganese(II) were 35.40, 32.73 and 33.37 mg/L and for iron(III) were 35.99, 36.95 and 37.87 mg/L. The results

showed that the removal of Manganese(II) and iron(III) was enhanced under the following optimal conditions: pH 5, contact time 35 minutes, sorbent weight 0.4 g, and temperature 50 °C. The Three sorbent materials could be effectively regenerated by using bidistilled water for more than five cycles. Adsorption kinetics followed the pseudo-first-order model, and Langmuir isotherm provided a good fit to the experimental data.

KEYWORDS: Adsorption, heavy metals, aqueous solutions, Activated carbon from watermelon rind, Borokly clay, Aswany clay.

1. INTRODUCTION

The levels of heavy metal contamination in water systems are increasing due to industrialization, climate change, and urbanization. Various sources contribute to this pollution, including mining residue, leachates from landfills, wastewater from both municipal and industrial sources, runoff from urban areas, as well as natural events like volcanic eruptions, weathering, and rock erosion. Over the past few years, the pollution of rivers and groundwater due to insecticides has become a prominent environmental concern with wide-ranging implications. The extensive application of agrochemicals in diverse agricultural activities, such as orchards and forests, has resulted in the widespread occurrence of insecticides in water sources. This contamination arises from various corridors, including surface runoff, filtered into the soil, wind erosion, aerial spraying, industrial effluents, and other sources. Consequently, pesticides are found in water across different countries globally **[1].** Toxic materials typically consist of heavy metals and organic pollutants, which have the potential to cause significant harm to water systems and soil. The ongoing problem of heavy metals pollution in water systems poses a serious threat to both human health and the environment **[2].** Several strategies have been developed for removing heavy metals from aqueous systems **[3].** The current therapy methods for heavy metal removal from polluted aqueous systems are often expensive and can sometimes result in the generation of additional toxic substances **[4].** The requirement for environmentally friendly, cost-effective, and non-toxic wastegenerating processes and separation techniques is evident. In this context, the adsorption process emerges as a promising solution. It is characterized by its low cost, operational simplicity, selectivity, and the potential for recovering the adsorbed substances **[5].** The adsorption method is highly suitable for removing heavy metals, both in low and high concentrations. It offers advantages such as easy separation under favourable conditions, the use of renewable adsorbents, a high adsorption load for heavy metals, and the production of zero sludge. These factors contribute to the effectiveness and efficiency of the adsorption process in heavy metal removal **[6-8].** According to the definition provided by the International Union of Pure and Applied Chemistry (**IUPAC**), activated carbon (**AC**) is characterized by a highly developed porous structure and possesses various surface functionalities. **[9].** The significant porosity of activated carbon allows for a vast surface area, which in turn facilitates effective adsorption. Additionally, the chemical properties of its surfaces contribute to enhancing the efficiency of adsorption processes. **[10,11].** Clays also were a naturally occurring finegrained particle found on the land face. It is primarily composed of water, metals compounds, silica, and small rocks **[12].** Clay with high surface area, porosity, and ion exchange capacity has been extensively utilized as highly efficient adsorbents for the removal of undesirable metals from hydrous systems, industrial and human societies for many centuries **[13-16].** The amendment of clay minerals can motivate several key properties that are important for adsorption. Studies have shown that the transformation of the clay can increase the pores size**[17-19].** This transformation of clay minerals is a suitable process to change their features

from being (water-loving) to more (waterrepelling). This transformation in wettability characteristics can be particularly beneficial for the removal of organic compounds from aqueous solutions**. [20,21].** The aim of work, **ACWR**, **BoC** and **AsC** samples were collected to adsorb some heavy metal ions from aqueous systems such as Mn(II) and Fe(III). Physical and chemical characteristics of the gained adsorbed materials were investigated by FT-IR, Xray fluorescence and SEM.

2. EXPERIMENTAL

2.1. Preparation of ACWR adsorbent.

The watermelon rind adsorbent material was collected from Zagazig area, Egypt. The collected samples washed with bidistilled water, and put in a blender to blend it. Small pieces of watermelon rind were then exposed to the sunlight for seven days in summer to allow their water content to evaporate. After this process, the desiccated watermelon rinds (**dWR**) were grindind to >50 mesh and stored in brown glass bottles. We prepare five flasks, each flask containing on one gram of dWR, 40 mL bidistilled water and different weights of KOH 0.5, 1, 2, 3 and 4 grams was added to the five flasks respectively. The mixtures were refluxed for one hour below their boiling point. Once dried, the mixtures underwent carbonization by being baked in a furnace

at temperatures 800 °C. Temperature was maintained for different durations of 30, 60, 90, and 120 minutes, respectively. This process resulted in the formation of (**ACWR**).To further treat the ACWR, was subjected to 0.1 N HCl and washed with bidistilled water until a neutral pH was achieved. Following this, the **ACWR** underwent an additional drying step in the incubator at a temperature 105 °C**[22]**. Finally, the was stored for future use .

The chemicals used in the study KOH, potassium permanganate, FeCl3. 6H2O, and HCl were obtained from Sigma and Aldrich.

2.2. Treatment of adsorbents BoC and AsC

Borokly clay and Aswany clay adsorbent material used in this study were collected from Abo-Elreesh (Aswan - Egypt). The collected samples were grinding, sifted to mesh size ≤ 100 mesh and then dried at 105 °C for 2 hours **[23].** The samples were then packed and stored.

2.3 Preparation of stock solutions Mn (II) and Fe(III)

Stock solutions (1000 mg/L) of Mn(II) and Fe(III) were prepared by dissolve 4.18 g of MnCl2.6H2O (M.Wt. 233.94 g/mol) and 4.84 g of FeCl3.6 H2O (M.Wt. 270.30 g/mol). The solutions were stored in a one litre measuring flask, diluted with bidistilled water to different concentrations as required .

2.4. Method of determination of Mn(II) and Fe(III) in solutions.

Mn(II) and Fe(III) were determined by dissolving Known amount of Mn(II) and Fe(III) into quick-fit glass bottle containing ACWR or BoC or AsC sorbents in 50 ml aqueous solution. The experiments were run out after controlling the solution at pH range 2 to 8. The kind of two metal ions on range of pH is documented **[24].** The amount of Mn(II) and Fe(III) adsorbed percentage of Mn(II) and Fe(III) removal by three sorbents was calculated by using equations. 1 and 2 **[25].**

$$
Qe = \frac{V(Ci - Ce)}{W}
$$
 (1)

 $\overline{(}$ $\frac{1}{\text{Ci}} \times$ Qe (mg/L) is the quantity of metal ions, V

is the volume (L), W is the material dose (g) , Ci (mg/L) is the metal concentration and Ce (mg/L) is the balance metal concentration in solution.

2.5 Isotherm studies

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The adsorption process on **ACWR**, **BoC** and **AsC** sorbents were determined using Langmuir isotherm and Freundlich isotherm models. The mathematical expression of the linearized pattern of the two models can be stated by equations 3 and 4 **[26].**

$$
\frac{1}{Q_e} = \left(\frac{1}{K_L \cdot Q_m}\right) \frac{1}{C_e} + \frac{1}{Q_m}
$$
 (3)

$$
Log Q_m = log K_f + \left(\frac{1}{n}\right) log C_e \tag{4}
$$

 C_e is the balance concentration (mg/L), Q_e (mg/L) and Q_m (mg/L) are the adsorption capacity at balance and the maximum load of adsorption, respectively, K_L is the constant (L/mg), while K_f (mg/g) and $1/n$ is the capacity of adsorption at unit .

2.6 Adsorption kinetics

The adsorption kinetics were studied by using psedo-first-order (Lagergren equation 5) [27] and psedo-second-order(equation 6) [28] to clarify the adsorption action of Mn(II) and Fe(III) ions on ACWR, BoC and AsC adsorbents to fit the experimental information.

$$
ln (Q_e - Q_t) = ln Q_e - K_1 t \tag{5}
$$

 Q_t (mg /L) is the amounts of metal ions adsorbed per unit mass of the adsorbent at time t (min.) and Q_e (mg/L) is the adsorption capacity at balance, and K_1 (1/min.) is the pseudo-first-order rate constant of the sorption process.

$$
\frac{\mathbf{t}}{\mathbf{Q}_{t}} = \left(\frac{1}{K_{2}.\,\mathbf{Q}_{e}^{2}}\right) + \left(\frac{1}{\mathbf{Q}_{t}}\right)\mathbf{t}
$$
\n(6)

 K_2 is the 2nd order rate constant.

3. RESULTS AND DISCUSSION

3.1 FT-IR spectra of ACWR, BoC and AsC.

The Infrared spectra were used to determined Based on the results shown in Figure 1, the raw **ACWR** adsorbent exhibited a wide and broad transmission band in the range of 3000-3654 cm-1 before adsorption. This broad band was

pointing to the O-H stretching mode of hydrogen-bonded hydroxyl groups attached to the structure or surfaceadsorbed moisture. [**29**-**31**]. The infrared spectrum of the raw **ACWR** adsorbent showed a distinct band at 1628 cm-1, which was rated to the C=O expansion vibrations of hydrocarbons present in the adsorbent material. Additionally, a small peak at 1112 cm-1 was observed, which was associated with the C-O expansion vibrations of the adsorbent. Interestingly, the intensity and position of this C-O expansion signal varied within the range of 1000-1100 cm-1, depending on the changes in the acid adsorption of the **ACWR** adsorbent. [**29**].The previously mentioned bands, the raw **ACWR** adsorbent also exhibited a wide peak in the range of 618-716 cm-1. This wide peak was associated with the double vibrations of C-H bending in the carbon structure and the physisorption of CO2 on the adsorbent surface. [**32**]. Bands of Borokly clay and Aswany clay (Fig. 2 and 3) at about 3600 and 3700 cm-1 were stamp OH vibration surface-adsorbed moisture [**33**]. The absorption peak at 1668 cm-1 may be refers to binding motion for H_2O which rated to adsorbed H_2O existing in clay [**34**]. The absorption peak at 1544 cm-1 is pointing to calcite vibration [**33**]. The range rated to Si-O occurs at 1023 cm-1, while the range between 920 and 909 cm-1

suggests Al-OH-Al distortion vibration [**33**]. Quartz ranges with Si-O and Si-O-Al vibrations were found in near to 794

and 690 cm-1, and ranges near to 520 and 450 cm-1 rated to elongation of the Si-O-Al bond [**33**].

Fig. 1: FT-IR spectra for (a) row Activated carbon, (b) after adsorption of Fe(III) and (c) after adsorption.

Fig. 2: FT-IR spectra for (a) row Borokly clay, (b) after adsorption of Fe(III) and (c) after adsorption of Mn(II)

Fig. 3: FT-IR spectra for (a) row Aswany clay, (b) after adsorption of Fe(III) and (c) after adsorption of Mn(II)

3.2 SEM of ACWR, BoC and AsC

The scanning electron microscope was used for characterization of **ACWR**, **BoC** and **AsC** before and after adsorption of $Mn(II)$ and Fe(III) ions (Fig. 4), (Fig. 5) and (Fig. 6).

The adsorption action involves mass group and presence of porous on the outermost layer or boundary of the adsorbent material. The surface of the **ACWR**, **BoC**, and **AsC** a dsorbents plays a vital role in increasing their overall surface area, as shown in Figures 4, 5, and 6 respectively. [**35**-**37**]. This increased surface area enhances the propensity for agglomeration between the adsorbent and the Mn(II) and Fe(III) ions. In other words, the porous and high surface area structure of the adsorbents facilitates the adsorption of the metal ions from the aqueous solution onto the solid surface. It is assumed that the rate-limiting step in the adsorption process is chemical adsorption, which may occur through electron sharing between the metal ions and the adsorbent material. [**38**].

Fig. 4: Scanning electron microscope for (a) row ACWR, (b) after adsorption of Fe(III) and (c) after adsorption of $Mn(II)$

Fig. 5: Scanning electron microscope for for (a) row Borokly clay, (b) after adsorption of Fe(III) and (c) after adsorption of Mn(II)

Fig. 6: Scanning electron microscope for for (a) row Aswany clay, (b) after adsorption of Fe(III) and (c) after adsorption of Mn(II)

3.3 X-ray fluorescence

X-ray fluorescence data (Table 1) for Borokly clays supported the presence of SiO3 58.80%, TiO2 3.09%, Al2O3 24.40%, Fe2O3 3.85%, CaO 0.21%, and Loss on ignition (Loi) 9.27%. For Aswany clay SiO3 55.2%, TiO2 2.4%, Al2O3 22.3%, Fe2O3 7.95%, MnO 0.04%, CaO 0.11%, K2O 2.02%, and Loss on ignition (Loi) 9.68%.

Table 1

X-ray fluorescence.

4.4 Factors affecting on removal of Mn(II) and Fe(III) from aqueous systems

4.4.1. Effect of pH.

The process were carried out with standard solutions at pH values 2, 3, 5 and 8. In case of ACWR, BoC, AsC sorbents, the results were showed in Fig. 7 (a and b) the removal percentages for Fe(III), Mn(II) increased by increasing of pH value of the solution until pH 5 (100%, 88.9%, 90.05%), respectively [**39**,**40**].

3.4.2 Effect of sorbents weight

50 mL from standard solutions from Fe (III) and Mn (II) ions, the pH of solutions was 5. Different weights from sorbents (0.1, 0.2, 0.3 and 0.4 g) were added to the standard solutions. The mixture was shacked. For **ACWR** The removal percentages for Fe(III) ion, which is nearly equal to 85.4 %, 87.5%, 93.4% and at (0.4 g) equal to 100 %. For Mn(II) ion, the removal percentage increased by increasing the weight of sorbent,90%, 91.5% 94.3% and maximum of removal 97% at sorbent weight (0.4 gm) Fig.8(a and b). In case of **BoC**, the extracting % of Fe(III) ion is increased by increasing the weight of sorbent with 76%, 52.3%, 78.2% and87% at (0.4gm). For Mn(II) ion, the removal percentage increased by increasing the weight of sorbent,58.75% ,59.37%, 84.2% and maximum of removal 89.21% at sorbent weight (0.4 gm) In case of **AsC**, , the extracting % of Fe(III) ion is increased by increasing the weight of sorbent with 62.5%, 65%, 85.3% and 88.6% at 0.4gm. For Mn(II) ion, the removal percentage increased by increasing the weight of sorbent,76.69%, 51.23%, 75.3% and maximum of removal 86.2% at sorbent weight (0.4 gm) [**36**].

Fig. 7: pH value of the solution (a) absorption of Fe(III) (b) absorption of Mn(II)

Fig. 8: Effect of weight of sorbents (a) absorption of Fe(III) (b) absorption of Mn(II)

3.4.3 Effect of contact time

50 mL from standard solutions Fe(III) and Mn(II) ions and 0.4 g **ACWR**, **BoC** and **AsC**. The pH 5 used for extracting of Fe(III) and Mn(II) ions. The optimum time at constant other conditions observed at 35 minutes for Fe (III) and Mn (II) with extracting percentages (95.23%, 91.15% and 91.91%) for Fe (III) And (97.88%, 79.32% and 91.89%) for Mn (II) Fig. 9 (a and b) [**41**].

Fig. 9: Effect of contact time (a) absorption of Fe(III) (b) absorption of Mn(II)

3.4.4 Effect of temperature.

50 mL from standard solutions from Fe(III) and Mn(II) ions 0.4 g **ACWR, BoC, AsC**, pH 5 and contact time 35 minutes used for extracting of Fe(III) and Mn(II) ions. At temperature 20, 25, 30, 35, 40, 45, and 50 °C. The

temperature at constant other conditions observed at 50 °C with removal percentage of Fe(III) were 95.1%, 91.5 and 90%. and For Mn (II) the removal percentages observed (97.1%,95.1% and 92.1%) Fig. 10 (a and b) [**42**].

3.4.5. Effect of concentration of metal ions

A series of standard solutions were prepared with various concentrations of Fe(III) and Mn(II) at 20, 30,40,50,60,70,80 and 90 mg/L. Each experimental was done for each concentration of metal ions at constant conditions (contact time 35 minutes, pH 5, temperature 50 \degree C and weight 0.4 g). Maximum removal of Fe (III) ions for at 30 mg/L equal 98.10%, 94.10% and 92.10%. Maximum removal of Mn (II) ion at 30 mg/L equal 96.10%, 84.20%, 86.20 %. Fig. 11 (a and b) [**42**].

Fig. 11: Effect of initial concentration of Fe(Ⅲ) and Mn(Ⅱ) (a) absorption of Fe (III) (b) absorption of

addsorption of $\overline{\text{H}}$ and $\overline{\text{H}}$ and $\overline{\text{H}}$ and $\overline{\text{H}}$ on $\overline{\text{H}}$ on $\overline{\text{H}}$ and $\overline{\text{H}}$ an <u>Mn (II)</u>

ACWR, **BoC** and **AsC** were less than unity. This suggests that physical adsorption is favourable for the adsorption of these ions on these particular adsorbents. To compare the maximum adsorption load of **ACWR**, **BoC** and **AsC** with other statement adsorbents for the removal of Fe(III) and Mn(II) ions, the data were recorded in Table 3 [**45**-**48**].

3.6 Adsorption Kinetics

Figures 13 (a, b, c, and d) depict the kinetics models for the adsorption of

3.5. Adsorption isotherm study

 $1/n$ can be determined by analysing the intercept and slope of graphs (Figures 12 a, b, c, d, e and f). In Freundlich model, the different values of reactivity of active sites (n) indicate different types of adsorption behaviour [**44**]. For values of 1/n greater than 1, the adsorption is held by chemical bonds, and for values of 1/n less than 1, the adsorption is favourable physical adsorption. For data in Table 2, it was observed that the 1/n values for the Fe(III) and Mn(II) onto ACWR, BoC and AsC clay. By plotting the logarithm of the difference between balance adsorption load (Qe) and the adsorption load at time t (Qt) against time (t), the rate fixed $(K1)$ and balance adsorption load (Qe) can be measured by the steep and intercept of the plot. In Table 4, (R2) for ACWR, BoC and AsC obtained using the 1st-order kinetic model, were greater compared to those obtained using the pseudo-2nd-order kinetic model. Additionally, the studied balance adsorption loads (Qe) from the pseudo-1st-order kinetic model closely match with the process data for ACWR, BoC and AsC. In summary, the results suggest that the adsorption kinetics of Fe(III) and Mn(II) onto ACWR BoC and AsC follow the pseudo-1st-order kinetic model.

3.7. Regeneration study

After conducting multiple cycles of adsorption and desorption, washing by bidistilled water, The removal percentage of Fe(III) on **ACWR**, **BoC** and **AsC** as shown in Fig.14a decreases by approximately 15.00%, 17.00% and 17.00%, hereafter five experiments. Similarly, the percentage removal of Mn(II) on **ACWR**, **BoC** and **AsC** (Fig.14a) decreases by 13.00%, 18.00% and 11.00%, after five cycles. In case of washing by 1N HCl, the removal percentage of Fe(III) on **ACWR**, **BoC** and **AsC** as shown in Fig.14b decreases by approximately 19.00%, 20.00% and 21.00%, hereafter five experiments. Similarly, the percentage removal of Mn(II) on **ACWR**, **BoC** and **AsC** (Fig. 14b) decreases by 17.00%, 19.00% and 20.00%, after five cycles. In case of washing by 1N NaOH, The removal percentage of Fe(III) on **ACWR**, **BoC** and **AsC** as shown in Fig.14c decreases by approximately 16.00%, 21.00% and 19.00%, hereafter five experiments. Similarly, the percentage removal of Mn(II) on **ACWR**, **BoC** and **AsC** (Fig.14c) decreases by 15.00%, 19.00% and 21.00%, after five cycles. Adsorption tests were carried out washing and without washing, by bidistilled water, 1N HCl, and 1 N NaOH. The results, depicted in Fig.14 (a,b,c and d), The information provided suggests that washing the adsorbents with bidistilled water was sufficient to make them usable. The primary mechanism for the adsorption approach appeared to be ion sharing. washing the metals from the adsorbents with bidistilled water was not show significant possible for adsorption. The decrease in adsorption capacity observed after each adsorption step was rated to the loss of binding sites on the adsorbent subjects. Nevertheless, Results can still score that the used adsorbents hypothetical be effectively reused for adsorption purposes, even after undergoing five experiments of adsorption, with only a slight reduction in their adsorption load. It is important to note that the provided information was based on the given statement or scenario, and specific experimental details, data,

and analysis techniques were not provided. Therefore, the interpretation and conclusions are limited to the information presented in the statement [**49**].

Fig. 13 Psedo 1st order kinetic model for (a) Fe(III), (b) Mn(II) and Psedo 2nd order kinetic model for (c) Fe(Ill), (d) Mn(II)

Table 2

Isotherm for the removal of Fe(III) and Mn(II) by Activated carbon from watermelon rind, Borokly clay, Aswany clay and adsorption capacity of prepared sorbents for as uptake

Isotherm parameters

Table 3

Comparison of Activated carbon from watermelon rind, Borokly clay,, Aswany clay and some other species.

Table 4

Kinetic Parameters

Application

The study examined the use of three adsorbent materials - ACWR, BoC, and AsC - for the adsorption of Fe(III) and Mn(II) ions from sub-river and underground well samples collected from different areas (Zagazig and Borg Alarab). The water samples were processed with 0.4 grams of the adsorbent materials at pH 5, with a contact time 35 minutes. The concentrations were measured before and after the removal process, (Table 5).The results indicate that ACWR was perfect in removing 98% of both Fe(III) and Mn(II) from the water samples. BoC was also forceful, removing 96% of Fe(III) and 95% of Mn(II). Similarly, AsC was forceful in removing 95% of both Fe(III) and Mn(II) from the water samples.

In summary, all three adsorbent materials - ACWR, BoC, and AsC - were found to be highly effective at removing Fe(III) and

Mn(II) ions from the surface water and underground water samples, with removal percentages ranging from 95% to 98%.

4. Conclusion

In light of these results , we can be concluded that our materials **ACWR**, **BoC** and **AsC** can be used efficiently in the removal of Mn(II) and Fe(III) from aqueous solutions. The results indicated this process dependent on pH value, weight of sorbents, contact time, temperature and initial concentration of the separated metal ions. The experimental data showed the final optimum conditions as the follows: contact time 35 minutes, pH 5, temperature 50 C, initial concentration of metals 30 mg/L and weight of **ACWR**, **BoC** and **AsC** were 0.4 gm. The order of the removal of the two heavy metal ions from aqueous solutions at the optimum conditions found as Mn(II)<Fe(III). The metal ions showed different behaviors by raising of the concentration of the metal ions towards

adsorption on **ACWR**, **BoC** and **AsC**. The experimental studies showed that ACWR, BoC and AsC can be used as inexpensive and effective substance for removing alarge amounts of toxic metals from aqueous solution.

List of abbreviations

ACWR Activated carbon from watermelon rind

BoC Borokly clay

AsC Aswany clay

FT-IR Fourier transform infrared spectroscopy

- XRF X-ray fluorescence
- M.wt. Molecular weight
- UV.vis Ultraviolet visible
- SEM Scanning electron microscope
- Fig. Figure
- % Percentage
- mg/L milligram per Liter
- bidis. Water bidistilled water

Table 5

Using Activated carbon from watermelon rind, Borokly clay and Aswany clay in the removing of Fe(III) and Mn(II) ions from aqueous samples

Fig. 14 Regeneration study (a)Washing with Dis.water (b) Washing with 1N HCl (c) Washing with 1N NaOH (d) Without Washing

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