International Journal of Research in Engineering and Science (IJRES)
ISSN (Online): 2320-9364, ISSN (Print): 2320-9356
www.ijres.org Volume 10 Issue 8 ǁ August 2022 ǁ PP. 682-687

Adsorptionstudies of Mn(II) using an effective low cost adsorbent -A comparative study

Daniel Kibami[1], Rokovikho Hesielie[1], Nikili Zhimo[1], Neilanuo Houzha[1]
[1]*Department of Chemistry, Kohima Science College (Autonomous), Jotsoma-797002, Nagaland, India*

Abstract
The removal of Manganese (II) from aqueous solutions using Bambusa vulgaris (common bamboo) and Fagopyrum esculentum Moench(FEMC) (common Buckwheat) as adsorbents was investigated. The two adsorbents are prepared by different methods and are chemically activated with 0.1 N HNO_3 and 0.1N H_3PO_4 respectively. Surface characterization of the synthesized adsorbents was done using scanning electron microscopy (SEM). The variable characteristics such as initial concentration, contact time and pH are recorded by batch adsorption technique. Adsorption data fitted well with all the adsorption isotherm models. However, Freundlich isotherm displayed a better fitting model than the other two isotherms because of the higher correlation coefficient of 0.9913 to 0.9980.This indicates the heterogeneity of the Mn(II) on the surface of which possessed different adsorption energy. The adsorption kinetics was studied using three simplified models and it was found to follow the pseudo-second-order kinetic model with a high correlation value of 0.9999-1, the high R^2 of this model almost equal to unity confirmed the applicability of the model.

Keywords: *carbonization; batch method; multilayer; correlation coefficient;*

Date of Submission: 18-08-2022 Date of acceptance: 02-09-2022

I. Introduction

With the advancement of science and technology the issue of water pollution has adversely increased with the influx of heavy metals into water bodies [Bailey et al. 1999]. Among the various toxic metals, Manganese is one trace element which exists naturally in the environment as solids and particles. In human beings the effects of Mn(II) occur mainly in the respiratory tract and in the brains[Kortenkamp et al. 1996]. Symptoms of Mn(II) poisoning are hallucinations, forgetfulness and nerve damage. In case of prolonged exposure to Manganese, it can lead to impotency as well [Banta et al.1977]. Thus the removal of metal ions particularly Mn (II) has become a burning issue worldwide and subsequently various experiments and measures were carried out for testing the presence of Mn (II) in water. Several treatment techniques including chemical coagulation [Mohammad et al. 2009], flocculation [Jordan et al. 1981], photo-degradation [Elmorsi et al. 2010], irradiation and precipitation [Crini et al. 2008] are not commonly used due to their high cost and also generally not feasible on large scale industries. In contrast, an adsorption technique is by far the most versatile and widely used in this regard. It has been reported that the adsorption onto activated carbon, has proven to be the most efficient and reliable method for the removal of many pollutants, including trace elements like manganese [Robinson et al. 2001]. Although commercial activated carbon is a very effective adsorbent, its high cost requires the search for alternative low cost adsorbents [Josefa et al. 2003]. In this regard, a large variety of low-cost adsorbents derived from agricultural and industrial wastes products which are readily available, biodegradable and simple by design [Feng-chin et al. 2006] and examined for effective removal of pollutants from water and waste water. The present study is an attempt to use Fagopyrum esculentum Moench(FEMC) (common Buckwheat) and Bambusa vulgaris (common Bamboo) as a non conventional low-cost adsorbent for removal of Mn(II) ions from aqueous solution.

II. Materials and Methods

2.1*Preparation of absorbent by indigenous method and by pyrolysis*

For this study, the initial carbonization is done at bamboo mission Dimapur,Nagaland,India. In this process, the whole bamboo culms are cut into a uniform size of 1m each so that it fits into the kiln, stacked horizontally through the door at the bottom. The door is then closed with bricks and plastered with mud on the outside for better insulation and to prevent leakage. The feed is fired through the opening at the top of the kiln and once the feed is ignited, the opening is closed. During the initial stages of firing, the openings in the wall of the kiln are kept open to create the required draft. Initially black smoke will be emitted from the opening at upper end, following the change to dense white fumes, openings are closed one by one starting from the top to bottom. Carbonization is achieved by maintaining the temperature at 400-500^{0}C by regulating the openings both in horizontal and vertical directions. All the openings are closed after 2 days so that air is not allowed to enter the kiln to prevent the charcoal from catching fire. Cooling is done for a day to reduce the temperature to 100^0C. The biomass removed from the opening at the bottom of the kiln are washed, dried and crushed and further subjected to chemical activation with 0.1N HNO_3 and 0.1N H_3PO_4. And for which the carbons were washed with double-distilled water to remove the excess acid and dried at 150^0C for 12hours. Another form of activated carbon in powder form are prepared by the pyrolysis of *Fagopyrum esculentum* Moench*(FEMC) (common Buckwheat).*The biomass were collected, washed, dried and crushed before carbonizing in a Muffle furnace electrically heated at 600^0C for 4 hours. The activated carbon prepared was cooled to room temperature and washed with deionized water until the effluent was clear in colour. Finally the synthesized carbon was dried in oven at 110^0C for 12 hours, chemically activated with 0.1N solution HNO_3 and H_3PO_4 respectively under similar conditions in order to modify the surface structure.These surface modified adsorbents are then observed under SEM and it is found to have a particle size in the range of 40-50 μm mesh.

2.2 *Preparation of Manganese (II) solution*

A stock aqueous solution of Mn(II) of 1000 mg/L was prepared by dissolving 3.6024 g manganese chloride tetrahydrate ($MnCl_24H_2O$ 99.99% purity) in 1000 ml distilled water. The pH of the working solution was adjusted to the desired value with 0.1M HCl and 0.1M NaOH using Elico-pH meter. Working solutions in the range of 5- 45 mg/L were prepared by further dilution. All chemicals used were of analytical reagent grade.

2.3 *Adsorption Studies of manganese (II) by Batch method*

Batch method is a technique used to study the adsorption capacity of activated carbons. In order to understand the adsorption behavior of Mn (II) ions effect of pH was studied ranging from 2-5.5. The effect of initial concentration was studied by varying Mn(II) concentrations between 5- 45 mg/L. The percentage removal of the manganese and the amount of manganese adsorbed were calculated by the following equations.

Percentage removal = $100\,\frac{(C_i - C_f)}{C_i}$

Amount adsorbed (q_e) = $\frac{(C_i - C_f)V}{M}$

where C_i and C_f are the initial and final equilibrium solution concentrations of the manganese (mg/ L), V is the volume of the solution (L) and M is the mass of the activated carbon (g). The data obtained have been analyzed for adsorption isotherms and various kinetic models.

III. Results And Discussion

3.1 *Surface Characterization*

Scanning electron microscope (SEM - JEOL, JSM 6360 LV) was used to know the surface texture and porosity of the sample. The SEM images clearly depict the pores and nature of the surfaces of activated carbon. [Dubnin 1989]. The SEM images of powder activated carbon are shown in figure 1.a-2.b. It is evident that there are larger numbers of pores present in the carbon activated by Nitric acid (HNO_3). Micrographs of FEMC (HNO_3) show some microporous structure with the pore size less than of 10 μm.

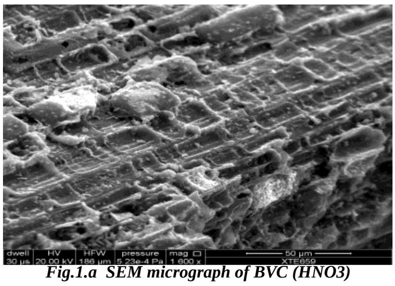


Fig.1.a SEM micrograph of BVC (HNO3)

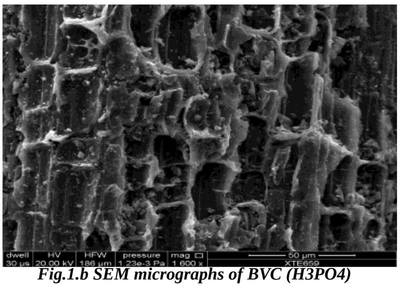
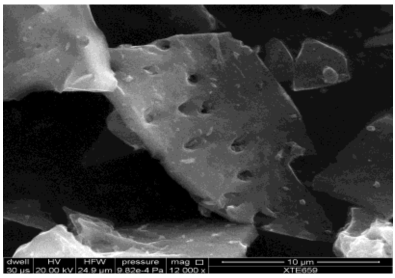


Fig.1.b SEM micrographs of BVC (H3PO4)



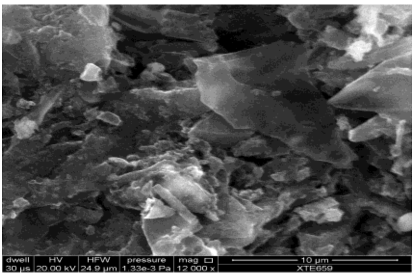


Fig.2.aSEM micrograph of FEMC (HNO3)   Fig.2.b SEM micrographs of BVC (H3PO4)

3.2 Effect of pH

The pH of a medium controls the magnitude of electrostatic charges which are imparted by the ionized Mn(II) molecules. As a result, the rate of adsorption will vary with the pH of an aqueous medium [Nasef et al. 2009]. The effects of pH on Mn(II) solution were investigated by varying the pH from 2-6 for 100ml of Mn(II) ions solution having a concentration of 10 mg/L and 1g of adsorbent. At pH -2 the removal was found to be minimum but it increases with increasing pH of Mn(II) solution. The maximum uptake of metal ion took place at pH 5.5–6 ± 0.1.The result in Fig. 3 shows that the maximum adsorption was observed at pH 5.5 for BVC (HNO_3) and BVC (H_3PO_4). At pH 5.5, the Mn(II) ions removed was 97.84% and 97.17% respectively. The maximum adsorption was observed for FEMC (HNO_3) and FEMC (H_3PO_4) at pH 6 with removal percentage of 95.78% and 95.61% respectively. The Mn(II) ions adsorption usually increased with the increase in pH. Lower adsorption of Mn(II) at acidic pH is probably due to the presence of excess H+ ions competing with the cation groups on the Mn(II)for adsorption site[Kannan 1991]. Experiments were not conducted beyond pH 6 as there is a possibility of metal hydroxide formation which might interfere with the biosorption process.

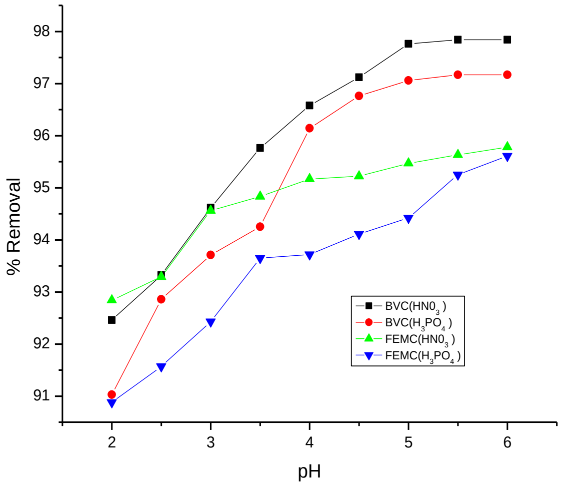


Fig .3 Effect of pH on percent removal of Mn(II) ions

3.3 Effect of concentration

The effect of concentration on the adsorption of Mn(II) ions wasstudied by varying the manganese in solution concentration between 5- 45 mg/L, wherein 100ml of Mn(II) ion solution, 1g of adsorbent was added for a contact time of 120min. The effect of the Mn(II) ion concentration on adsorption depends on the immediate relation between the manganese concentration and the available binding sites on an adsorbent surface [Tan et al. 2008]. Fig.3 shows the effect of Mn(II) ion concentration with different adsorbents [BVC (HNO_3), BVC (H_3PO_4), FEMC (HNO_3) and FEMC (H_3PO_4). The relevant data shows that with the increase in initial concentration of the Mn(II) ions, the amount adsorbed exponentially increases while the percentage removal exponentially decreases, which may be due to the saturation of adsorption sites on the adsorbent surface [Tan et al. 2009]. At low concentration, there will be unoccupied active sites on the adsorbent surface and with the concentration increase, the active sites required for adsorption decreases. However, increase in the Mn(II) ions concentration will cause an increase in the loading capacity of the adsorbent and this may be due to the high driving force for mass at a high ion concentration [Ayub et al. 1998]. The variation of percent removal of Mn(II) ions with increasing concentration is shown in Fig.4. The results indicate that when BVC (HNO_3) is used an adsorbent, the percent removal decreases from 98.69% to 92.89% while the amount adsorbed increases from

0.4934 to 4.1802. However, in the case of BVC (H_3PO_4), FEMC (HNO_3) and FEMC (H_3PO_4), the percent removal decreases from 98.40 to 89.73, 98.25 to 88.91 and 98.17 to 88.49 respectively. Thusunder identical experimental conditions, the order of adsorption capacity of the various adsorbents is as: BVC (HNO_3)> BVC (H_3PO_4)> FEMC (HNO_3)> FEMC (H_3PO_4).

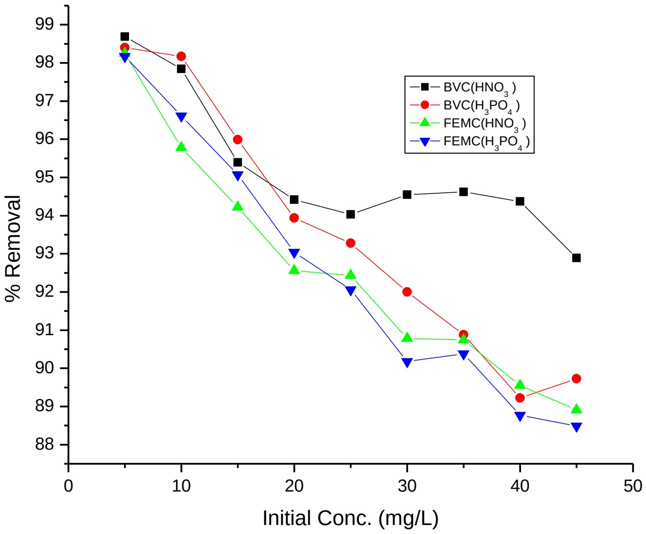


Fig.4.Variation of percent removal of Mn(II) ions with increasing initial concentration

3.4 Adsorption Isotherm study

An adsorption isotherm gives the relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution [Langmuir 1918].Various adsorption isotherm models are employed in this study to describe the experimental adsorption isotherm [Langmuir 1918, Javed et al. 2007].

3.5 Langmuir adsorption model

The Langmuir adsorption model suggests the formation of monolayer adsorption and also the surface is energetically homogeneous [Langmuir 1918]. The Langmuir equation which is valid for monolayer adsorption onto a surface is given below [Javed et al. 2007]

$$q_e = \frac{K_L C_e}{1+a_L C_e}$$

The linear form of the Langmuir equation can be represented by,

$$\frac{C_e}{q_e} = \frac{a_L}{K_L} C_e + \frac{1}{K_L}$$

Where q_e is the amount of Mn(II) ions adsorbed (mg/g) and C_e is the equilibrium concentration of Mn(II) ions in the bulk solution (mg/L). a_L/K_L gives the theoretical monolayer saturation capacity, q_m (mg/g), and $1/K_L$ is the Langmuir constant related to energy adsorption capacity. The essential characteristics of Langmuir equation can be expressed as

$$R_L = \frac{1}{1+a_L C_i}$$

where C_i(mg L^{-1}) is the initial adsorbate concentration and a_L(L mg-1) is the Langmuir constant related to the energy of adsorption. The value of $R_L$indicates the shape of the isotherms to be either unfavorable (R_L>1), linear (R_L= 1), favorable (0<R_L<1) or irreversible (R_L= 0). The coefficient correlation values were obtained, with R^2 value of 0.9607, 0.9590, 0.9397 and 0.8591 for BVC (HNO_3), BVC (H_3PO_4), FEMC (HNO_3) and FEMC (H_3PO_4) respectively, suggesting the favorability of the Langmuir isotherm for the system under observation. The values of monolayer capacity (q_m) and Langmuir constant (K_L) have been evaluated from the slope and intercept of these plots (Table 1), which suggest that BVC (HNO_3) has the maximum value of monolayer adsorption capacity (q_m) as well as energy of adsorption (K_L). The adsorbents under study showed that the maximum monolayer adsorption capacity and energy of adsorption follows the order BVC (HNO_3) > BVC (H_3PO_4) > FEMC (HNO_3) >FEMC (H_3PO_4).The results for separation factor (R_L) from table 1 show R_L< 1 in all the cases, which indicates a favorable Langmuir isotherm for the adsorbents used in this study

	Frendulich Isotherm				Langmuir Isotherm				Temkin Isotherm			
	R^2	Log K	1/n	n	R^2	Q_{max}	K_L	R_L	R^2	B_T	Bln(A)	A_T
BVC (HNO_3)	0.9991	0.9712	0.689	1.554	0.9607	57.714	0.942	0.0179	0.9524	0.427	2.478	410.826
BVC (H_3PO_4)	0.9913	0.674	0.625	1.586	0.9590	30.196	0.585	0.0254	0.9718	0.334	1.678	271.963
FEMC (HNO_3)	0.9933	0.654	0.656	1.453	0.9397	56.497	0.797	0.0202	0.9253	0.326	1.369	75.324
FEMC (H_3PO_4)	0.9980	0.379	0.694	1.627	0.8591	14.088	0.135	0.0305	0.9367	0.354	1.296	59.818

Table 1.Adsorption isotherm parameters for Mn2+ adsorption on synthesized adsorbents.

3.6 Freundlich adsorption model

Freundlich isotherm is an empirical equation describing the heterogeneous adsorption and assumes that different sites with several adsorption energies are involved[Freundlich et al. 1939].The linear form of the Freundlich equation is shown below.

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

The slope 1/n gives adsorption capacity and intercepts log k gives adsorption intensity. Freundlich shows very high regression correlation coefficients R^2 values of 0.9991, 0.9913, 0.9933 and 0.9980 for BVC (HNO_3), BVC (H_3PO_4), FEMC (HNO_3) and FEMC (H_3PO_4) respectively. This indicates the applicability of the Freundlich isotherm for the system under observation.The most favorability for Manganese (II) ions adsorption was observed in BVC (HNO_3) which showed the highest $1/n$ value.The highest adsorption capacity (K) was shown by BVC (HNO_3). The values of $q_e$calculated from Freundlich isotherm were all close to experimental values as evident from low chi-square values. This satisfies the Freundlich isotherm model for the adsorption of manganese (II) ions, indicating the applicability of multilayer coverage of the manganese (II) ions on the surface of adsorbent and also the heterogeneous distribution of active sites on the adsorbent.

3.7 Temkin isotherm model

Temkin isotherm model predicts a uniform distribution of binding energies over the population of surface binding adsorption [Temkin et al. 1940]. The Temkin isotherm is applied in the following form

$$q_e = \frac{RT}{b_T} \ln (A_T.Ce)$$

The linear form of Temkin equation is

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \qquad ; q_e = \beta \ln\alpha + \beta \ln C_e$$

$$\text{Where, } \beta = \frac{RT}{b_T}; \ \alpha = A_T$$

T is the absolute temperature in Kelvin, R is the universal gas constant, 8.314 J/mol K, b_T is the Temkin constant related to heat of sorption (J/mg) and A_T the equilibrium binding constant corresponding to the maximum binding energy (L/g) The isotherms indicate that adsorption increases with an increase in equilibrium concentration of the metal ion. The value of the correlation coefficient (R^2) of Temkin model ranges from 0.9253–0.9718. It is evident from table 1 that BVC (HNO_3) has the maximum value of heat of sorption (b_T) and the maximum binding energy (A_T), which suggest the best adsorbent among the other adsorbents under study. However the values of $q_e$calculated from Temkin isotherm were not close to experimental values. Therefore, it was observed that the adsorption of manganese (II) ions did not fit Temkin isotherm as closely as Langmuir and Freundlich models.

IV. CONCLUSION

Adsorption studies of Mn(II) ions on activated carbons was studied using batch method, the parameters considered were effect of pH, effect of concentration of solution and effect of contact time. The results indicates that removal of Mn(II) ions increased with the increase of contact time and pH . On the contrary, the percentage of removal for manganese ion decreased with the increase in concentration of the standard Mn(II) ions solution. Maximum adsorption at acidic pH suggest the fact that low pH leads to an increase in H^+ ions on the carbon surface, resulting in significantly strong electrostatic attraction between positively charged adsorbent surface and manganese ions. The equilibrium adsorption data was analyzed using Langmuir, Freundlich and Temkin isotherms. Out of three isotherm models studied, Freundlich model shows best fit with a correlation coefficient of 0.9913 to 0.9991 indicating heterogeneous and multilayer adsorption. Among the four low-cost adsorbents under study, the order of adsorption capacity of the various adsorbents is as follows: BVC (HNO_3) > BVC (H_3PO_4) > FEMC (HNO_3) > FEMC (H_3PO_4). BVC (HNO_3). It may be concluded that the chemical structure of the activated carbon were found to be influenced markedly with its activation scheme and thus chemical activation by nitric acid is far more better than phosphoric acid.

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