Removal of Zinc(II) from municipal wastewater using chemically modified activated carbon developed from Rice husk and Kikar charcoal

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Abstract*-- Heavy metals in municipal wastewater are of utmost concern for researchers and environmental agencies due to their adverse effect to the ecosystem. Various technologies were practiced for the removal of heavy metals; however, adsorption is one the most interesting technique for its low cost, simple operation and reasonable efficiency. In this study, removal of Zinc (II) from municipal wastewater in Quetta city of Pakistan was investigated by using activated carbon (AC) developed from Rice Husk (RH) and Kikar Charcoal (KC). Char were made by heating KC and RH in a tubular reactor at 700 ºC under N_2 gas flow. Furthermore, Char material obtained were activated using H2SO4 as an activating agent to increase the surface area and porosity of the char materials. The biochar adsorbents were characterized using SEM, EDX and BET techniques. To identify the efficiency of adsorbents, the wastewater samples collected from Shahbaz town area of Quetta city were treated using different particle size of AC (180 and 300 µm) and varying adsorbate dose (0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 g/50 mL), pH of the solution (3, 4, 5, 6, 7), respectively. The results showed that increase in the mass of adsorbents had a direct relation with the removal efficiency of Zn(II). The maximum removal efficiency for zinc (II) was found to be 99 % and 72.34 % for KC and RH based ACs at adsorbent dose 0.7 g/50mL and pH 6, respectively. A small difference has been observed between the efficiencies of both ACs this was due to the difference between their surface area and porosity. While studying isotherm models the data was best fit with Langmuir isotherm model. The amount of zinc in the treated wastewater was recorded well enough under the standard limits provided by Environmental protection agency (EPA). This technique of treating municipal wastewater by using inexpensive biomass as adsorbent found to be very efficient and environmental friendly.

***Keywords*- Activated carbon; Adsorption; Kikar Charcoal; Rice Husk; Ecosystem**

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I. INTRODUCTION

The presence of heavy metals and other contaminants in wastewater is one of the growing threat to underground water reservoirs, agriculture, human health, and environment. Srivastava & Majumder [1] defined heavy metals as "the elements having atomic weights between 63.5 to 200.6 and a specific gravity greater than 5". Different heavy metals in wastewater are unnecessary, persistent and toxic to human health in many ways [2]. Zinc is one of these trace elements, which is non-biodegradable and becomes part of food chain [3]. Its limited amount is essential for good health; however, increased amount causes many adverse effects including lethargy, depression, some neurological problems, vomiting, skin irritation and many more [5]. Many techniques such as filtration, sedimentation, coagulation, flocculation, biological and chemical treatments are used for wastewater treatment, but having some limitations such as increased cost and a heavy amount of sludge production may decrease the effectiveness and popularity of such processes [4]. Hence it requires an alternate process which gives better results in terms of cost-effectiveness, operation and sludge disposal. "Adsorption" is one of the most interesting techniques covering theses all requirements with easy design and operation. Also, adsorbents can be regenerated by desorption [5]. The selection of adsorbents for AC is of main concern, as depletion in coal reserves in the world are causing high price of adsorbents as well. Hence, the local made inexpensive adsorbents will be one of the best options. For example, Dias et al,. [8] investigated different waste materials for AC preparation and Kongsuwan et al,. (2009) studied the preparation of AC from eucalyptus bark. Many studies have been made to prepare low-cost ACs from locally available materials [5]. Sud et al,. [10] stated many agricultural wastes as potential ACs. Iqbal et al,. [11] used petiolar felt-sheath of palm for removal of heavy metals from wastewater. A similar study was done by Seki et al,. [12] by using coniferous barks as adsorbents. Also, Babel & Kurniawan [14] studied low-cost adsorbents for contaminated water treatment. So, low- cost adsorbents for AC are of keen interest to researchers [12]. Recently agricultural wastes and by-products gained much attention due to their very low cost, abundant availability, environmentally friendly characteristics and waste management (disposal) [13], [8]. Rice is the 11th most abundant crop of Pakistan by production and Kikar is abundantly available in Balochistan (District Lasbella), Southern Punjab and Sindh province of Pakistan. Locally available materials for adsorbents give economic, environmentally friendly and best waste management results.

In current study, RH and KC are used as adsorbents to prepare ACs due to their abundant availability in Pakistan. RH is one of the waste product of rice mills and almost 0.23 tons of RH is produced while processing 1 ton of rice [14]. During 2015-16 rice production in Pakistan was reported 6,811 thousand tons [15]; which give about 1566530 tons of RH in the country. These figures give an excellent opportunity to use RH as adsorbent at low cost and at the same time, it gives the best solution of a waste disposal problem. RH contains cellulose (32.24%), hemicellulose (21.34%), lignin (21.44%), extractives (1.82%), water (8.11) and mineral ash (15.02%) [16]-[17] is a tree belongs to Mimosaceous family with the binomial name "Vachellia nilotica" [18], [19]. It has 77% volatile matter, 22.40% fixed carbon and 0.60% ash contents in dry form while having volatile matter (77.46%) and fixed carbon (22.54%) in dry and ash free form by weight [20]. While its ultimate analysis results show that by weight it contains carbon (45.89%), hydrogen (6.08%) and oxygen (47.43%) in dry form; while in dry and ash free form it contains carbon (46.17%), hydrogen (6.12%) and Oxygen (47.72%) [20]. Low cost and easy availability of agricultural waste as adsorbents gain the considerable attention of researchers. In this study, RH and KC were used to remove Zn (II) from municipal wastewater in Quetta city of Pakistan. As Pakistan is the 11th largest rice producer and 5th largest rice exporter country worldwide [15]. Also, Kikar is abundantly available in Sindh, Punjab, and Balochistan (Lasbella district), which make it inexpensive. These both materials are generally burnt as firewood for domestic and commercial purposes creating many environmental problems too [14].

Following above consideration we aimed to prepare activated carbon from KC and RH. The activation was conducted in two step process: using tubular reactor to prepare char, and secondly activation of char into KC and RH activated carbons using H_2SO_4 as a chemical agent. The efficiency of both the activated carbons were identified by treating municipal wastewater with different particle sizes (180 and 300 µm) of KC and RH. Experiments were conducted against variable dose, pH and time of contact. To analyse the proficiency of adsorbents the samples were characterized before and after adsorption. Wastewater samples were collected from Shahbaz town area of Quetta city, where various sewerage lines combine together. Twelve samples of wastewater were used in the current study for two different particle sizes of AC (180 and 300 µm) and three different doses of adsorbents (0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 g/50 mL).

II. Materials and methods

Following steps were followed for the preparation of KC and RH based activate carbons (Fig. 1).

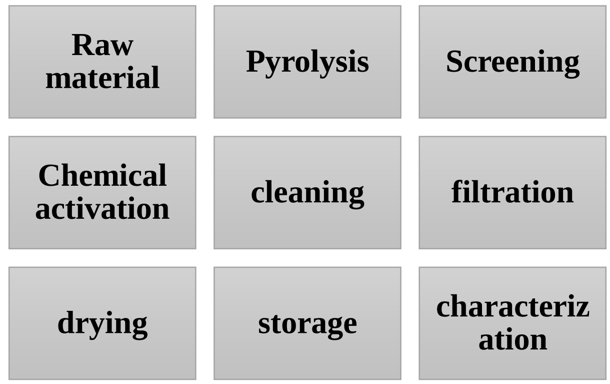

Fig. 1. Process fow chart from activated carbon preparation to wastewater treatment

A. Materials

All chemicals and reagents used were of analytical grade and were purchased from Merck chemical Inc. GmbH. Kikar charcoal and rice husk (Fig. 2) were obtained from local seller and distributor of wood charcoal at Quetta, Pakistan.

Fig. 2. Raw material used as an adsorbent for activated carbon (a. Rice Husk, b: Kikar Charcoal)

B. Preparation of activated carbon

1. Heating

RH was obtained from Rice mills in Punjab and KC from local market of Quetta city of Pakistan shown in Fig. 2 (a & b). The tubular furnace was used for heating of RH at 700 ºC for 2 hours and heating rate @ 10 ºC/min, with continuous nitrogen flow inside the reactor.

2. Grinding and sieving

Once washed and cleaned using deionized (DI) water, biochar was ground and passed through different sieves to get desired particle size of 180 and 300 µm. Particle size distribution was conducted using different sieves of 50 and 80 mesh screens were used in the current study and the screened particles obtained were suitable for preparation of ACs.

2. Pyrolysis of KC and RH into biochar

Slow pyrolysis technique was conducted inside a tubular reactor under N_2 flow at 700 ^oC for 2 h to convert KC and RH into biochar. The rate of temperature increase was kept constant at 10 ^oC/min. In order to avoid any contamination N_2 gas was initially flushed through the reactor to release any oxygen if present.

3. Chemical activation

Biochar obtained were then further treated with 3% v/v solution of H_2SO_4 for chemical activation. RH and KC particles were soaked with H_2SO_4 solution for 15-18 hours. After that these ACs were washed with distilled water three times to remove free acid completely. The washed AC was dried by keeping in an oven at 105 ^oC for 4 h or until a constant weight obtained.

C. Batch experiments

Twelve different municipal wastewater samples were collected for current study from Shahbaz town area of Quetta city. In Shahbaz town, main sewerage lines meet together by passing through the populous area of the city, making the location more suitable for collection of the samples [21].

All the batch experiments were conducted using a laboratory scale batch incubator shaker at 25 ^oC and 150 rpm. Three sets of batch experiment were performed to get the optimum results. In the first set, the effect of adsorbent composition was studied on the removal efficiency of Zn(II), subsequently in the second set, the effect of particle size was investigated on the removal efficiency of Zn(II). Similarly, experiments were repeated with variable pH (3, 4, 5, 6, and 7). All the experiments were repeated in triplicate and the optimum values were reported here. For rest of the experiments the optimum pH value was kept constant for the removal of Zn(II) [22]. As reported earlier at lower pH, there is net positive charge on the biomass cells, which results in higher electrostatic repulsion between the metal ions and the H^+ion during the uptake of metal ion [23]. Whereas at higher pH, there is net negative charge on the biomass, which results in a decrease in the electrostatic repulsion and thus increases the biosorption. A similar trend was reported for the biosorption of Zn (II) on Neem biomass [24]. The whole process was done at ambient temperature.

III. RESULTS AND DISCUSSION

Appendixes, if needed, appear before the acknowledgment.

A. Characterization

1. Scanning electron microscopy (SEM)

SEM images of KC and RH activated carbons were captures at 1000 (before activation) and 7000 (after activation) magnifications. Fig. 3 (A) & (B) shows the SEM images of KC and RH in which visible porous structure after chemical activation of the adsorbents can be seen. In this investigated the pine char structure in order to determine the effect of pyrolysis pressure and heating rate. The porous holes of KC and RH activated carbon are seems to be bigger with clearly defined thin cell walls. The pores are suspected to be formed by the release of volatiles during the pyrolysis. More volatiles are released because of the temperature effect during pyrolysis.

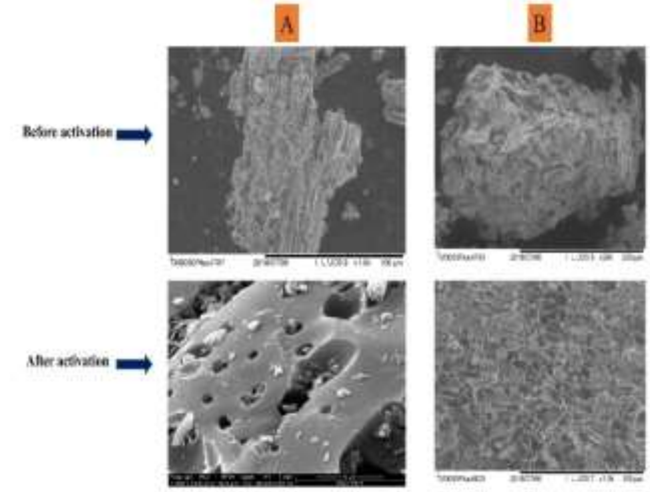

Fig. 3. SEM images of A) KC and B) RH before and after chemical activation

2. Electron dispersion x-ray (EDX) and mapping

Elemental composition of the adsorbents before and after adsorption is very important in terms of identifying the efficiency of an adsorbent. EDX graph showed the elemental composition of KC, with 88% C, 6.54% O, 0.57% Si, 1.67% Cl and 3.21% K (Fig. 4).The percentage of Mn and O suggested the presence of MnO_2 on Adsorbent. Insignificant Si percentage suggested that the surface had been covered to the good extent. The presence of traces of Cl and K was due to trapping of these ions. The graph before adsorption doesn't shows any peak for Zn(II) which is visibly appeared in the graph taken after adsorption of Zn(II). The Zn(II) uptake was calculated to be more than 9 wt. %.

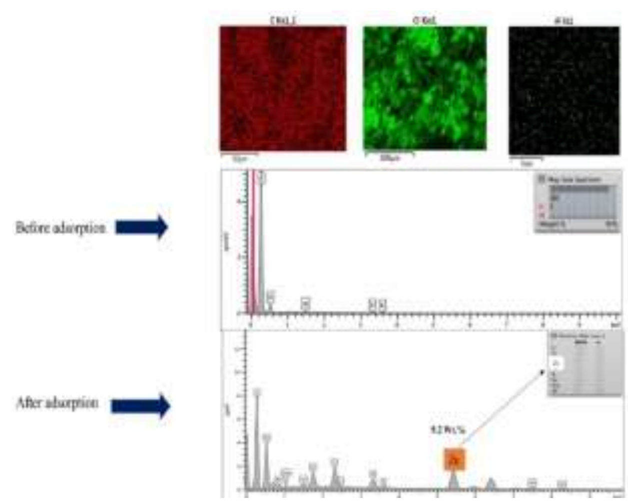

Fig. 4. EDX graph and mapping of KC before and after adsorption

3. Brunauer–Emmett–Teller (BET) Surface area

The BET surface area of both KC and RH were calculated before and after chemical activation. A remarkable increase in the surface area of both KC and RH were observed. The surface area of It was noticed that the surface area of KC and RH were increased from 254 m^2/g and 134 m2/g to 534 m^2/g and 411 m^2/g, respectively. This improvement in surface area was due to the cleaning effect of acid during the activation process. It was also noticed that addition of the acid into the char material have removed the unwanted associated components from the surface of KC and RH. Furthermore, more thermal cracking was assessed at higher temperature leads to release more gaseous products [24]. During the release of gas, the surface of KC and RH deforms and creates more pores.

B. Adsorption experiments

The removal efficiency of AC developed from RH and KC for Zinc (II) metal ions gave different values for changing adsorbent dose and particle size of ACs by using following equation;

$$\%\ \text{Removal} = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

Where C_0 is the initial concentration of Zinc and Ce denotes final concentration. Initial and final concentration of the samples were analyzed using flame atomic adsorption spectrophotometer (Perkin Elmer AAnalyst 100).

C. Effect of time

Effect of time is very important when calculating the isotherm studies and to get the adsorption equilibrium. Fig. 5 shows the effect of time against the removal of Zn(II). The removal of Zn(II) was very rapid at start and achieved equilibrium at 105 min. Sample were left agitated until the constant removal was obtained. The removal of KC obtained was 99% and the removal for RH was 72 %. The contact time required to achieve equilibrium adsorption was later followed for rest of the experiments.

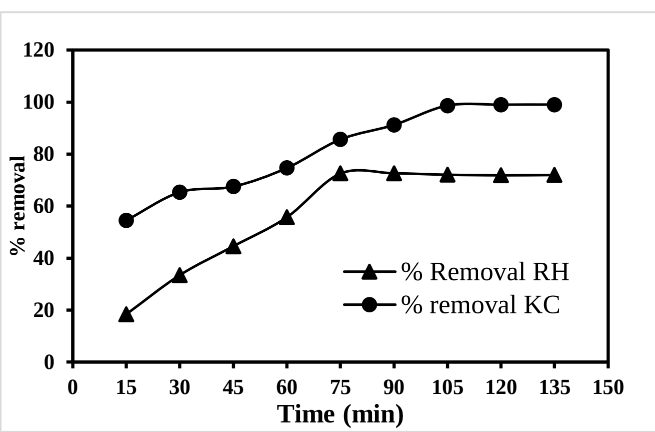

Fig. 5. Effect of contact time against removal of Zn(II)

D. Effect of adsorbent dosage with variable particle size

The effect of AC dosage on the removal of Zn(II) was assessed by treating prescribed amount of adsorbent with 50 mL of wastewater in a laboratory scale shaker with 180 rpm agitation speed. Initially the removal efficiency of Zn(II) was calculate using the particle size of 180 µm with adsorbent dose range of (0.1-0.7 g/50 mL). For RH based AC, the removal efficiency increased with increase in AC dosage from 0.1 g to 0.7g from 35 % to 99 %, respectively. However the maximum removal obtained for RH was 72.26 % which was comparatively less (Fig. 6). The efficiency of ACs at a particle size of 300 µm of RH and KC based ACs was also checked with different doses in the range (0.1 – 0.7 g/ 50 mL). For RH based AC, the removal efficiency increased with increase in AC dosage from 0.1 g to 0.7g from 31 % to 93.54%, respectively. However, the maximum removal obtained for RH was 68.21% which was comparatively less. Once compared with the different particle size the maximum removal efficiency obtained was for 180 µm and a dose of 0.3 g/50 mL for KC and 0.7 g/50 mL for KC (Figure 7). Also, KC-based ACs gave better results for Zinc removal (99 %) as compared to KC (69 %). The adsorption capacity of rice husk very much depends on the surface activities-in other words, the specific surface area available for solute-surface interaction, which is accessible to the solute [16]. The % removal was higher in the case of maximum dosage of AC used was due to the reason there were more active sites available for the Zn(II) ion to get absorbed. Whereas, with a low amount of AC there was fight against the heavy metal ions with the less available sites for adsorption.

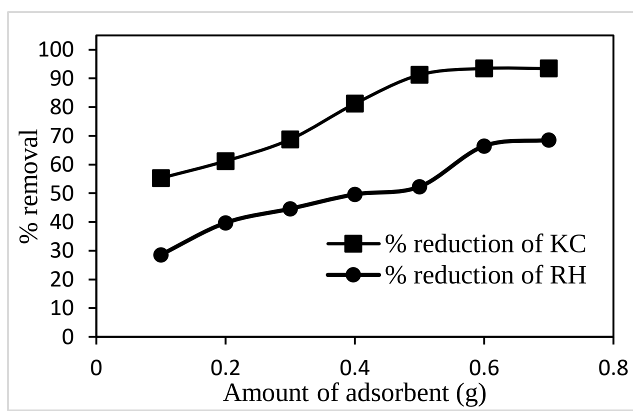

Fig. 6. % Removal efficiency vs adsorbent dose at 180 µm particle size of activated carbon

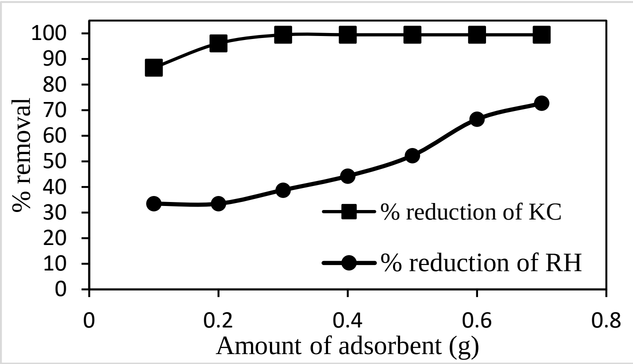

Fig. 7. % Removal efficiency vs adsorbent dose at 300 µm particle size of activated carbon

TABLE I

Summary for Zinc (II) removal efficiency of RH and KC based adsorbents at different particle size and doses

Activated carbon size (µm)	Type of adsorbent	Dose (g/ 50 ml)	% Removal
180	Rice Husk	0.1	33.35
		0.5	68.54
		0.7	72.24
	Kikar Charcoal	0.1	38
		0.5	98.68
		0.7	99
300	Rice Husk	0.1	32.1
		0.5	58.52
		0.7	68.82
	Kikar Charcoal	0.1	36
		0.5	60
		0.7	93.24

E. Effect of pH

It is known that the sorption of heavy metal ions by solid substrates depends on the pH of the solution. Mishra *et al*. [22], suggested that the contents of the active functional groups, amino acids and metal oxides in rice husk, may have an effect on the uptake process. Adsorption of Zn(II) increases with the increase of pH values (Fig. 8). Rice husk and Kikar charcoal activate carbons could exhibit a hydration shell at lower pH positively charged by the hydronium ion, H+, in the solution. This restricted the uptake of Zn(II) ions. Removal of Zn(II) ions increases with increasing pH values. At moderate to high pH values, zinc ions exist as Zn^{2+}, $Zn(OH)^{+}$ and $Zn(OH)_2$, which are favorable species for adsorption of trace zinc ions.

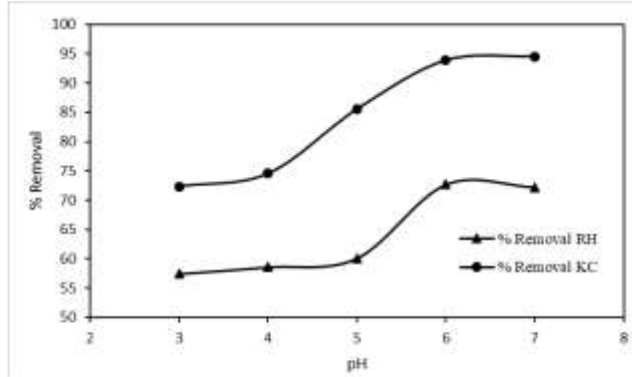

Fig. 8. Effect of pH on the removal of Zn(II)

F. Isotherm studies

To further study the validity of the data, different isotherm models were studies and the best fit model is shown in Fig. 9. Following linearized langmuir equation (2) was used to calculate the q_{max} and R^2.

$$qe = \frac{q_{\max}.K_L.C_e}{1+K_L.C_e} \quad (2)$$

Where q_{max} (mg/g) is the maximum capacity of adsorbent. KL (L/mg) is the adsorption equilibrium constant which is related to the energy of adsorption. qe (mg/g) is the adsorption capacity of at equilibrium.

The R^2 value for KC is equal to 0.99 % whereas the R^2 for RH is calculated to be 0.98. The q_{max} was calculated to be 24 mg/g for KC and 12.16 mg/g for RH, respectively. Langmuir isotherm accounts for the surface coverage by balancing the relative rates of adsorption and desorption (dynamic equilibrium). Adsorption is proportional to the fraction of the surface of the adsorbent that is opened while desorption is proportional to the fraction of the adsorbent surface that is covered [23].

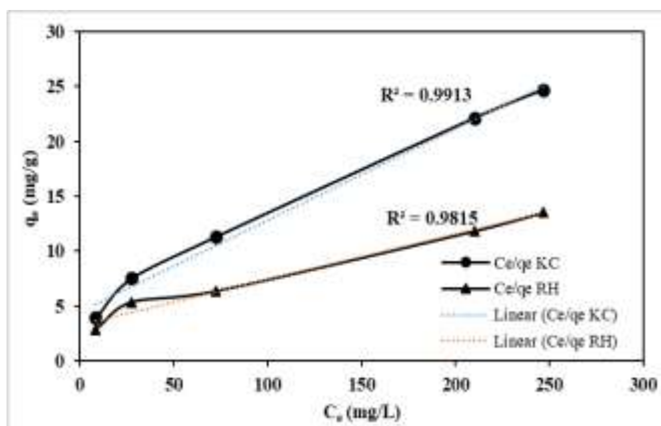

Fig. 9. Langmuir isotherm model for KC and RH

IV. Conclusion

The removal efficiency of rice husk and kikar charcoal after chemical activation has successfully increased to 72.24% and 99% with particle size 180 µm, pH 6, and adsorbent dose 0.7 g/50 mL, respectively. Langmuir isotherm was identified to be the best fit with the data obtained. The value of q_{max} of KC and RH were calculated to be 24 mg/g and 12.16 mg/g. The improved surface area after activation from 254 m^2/g and 134

m^2/g to 534 m^2/g and 411 m^2/g was the main reason which contributed for the improved efficiency of the adsorbents for the removal of Zn(II) . The abundance of selected materials for AC makes availability very easy in Pakistan. The use of this material not only beneficial for wastewater treatment but also gives an alternate solution to waste disposal at the same time. The process is simple and cost-effective; however further improved results can be checked at different temperatures.

V. Acknowledgment

These experiments were carried out at central laboratories of Department of Chemical Engineering, BUITEMS and Pakistan Council for Scientific and Industrial Research (PCSIR) laboratories Quetta, Pakistan

VI. References

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