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Determination of Point Zero Charge (PZC) of Homemade Charcoals of Shorea Robusta (Sakhuwa) and Pinus Roxburghii (Salla)

Manoj Khanal[1], Debendra Rai [1], Rajendra Khanal[2]
[1]Central Campus of Technology, Tribhuvan University, Dharan, Nepal, Nepal
[2]Associate fellow, Nepal Academy of Science and Technology, Khumaltar, Lalitpur, Nepal

Ajaya Bhattarai[3]*
[3]Department of Chemistry, Mahendra Morang Adarsh Multiple Campus, Tribhuvan University
Biratnagar, Nepal

Abstract— **The point of zero charge (PZC) values of adsorbents predicts the ease of substrate to adsorb potentially harmful ions like those of pesticides, dyes, etc. Charcoals of locally available woods of *Shorea robusta* (Local name: *Sakhuwa*) and *Pinus roxburghii* (Local name: *Salla*) possess at home. For reference, commercial activated charcoal was also taken. The points of zero charge of charcoals of all adsorbents under study were determined by a well-known pH drift method. The PZC of *Sakhuwa*, *Salla* and commercial charcoals were 2.9, 4.1 and 5.0 respectively. The analyzed PZC values predict that the charcoals of *Sakhuwa* and *Salla* have adsorption capacity in the acidic region and attract anions towards them.**

Keywords— ***Adsorbents, Charcoal, pH drift method, Point zero charge***

I. INTRODUCTION

For centuries, charcoal was commonly used to cure an array of human and beastly ills. Charcoal is being used for centuries, and its used has declined since 1950 after the tremendous growth of the drug industry (1). Charcoal is simple to prepare with local inexpensive technologies, it does not possess harmful side-effects, and non-allergenic (1 - 2). Both animal and plant products are used for the preparation of charcoal (2 - 3). Charcoals from plant products are believed to be better compared to animal bones for medicinal applications. Commercially, plant products used for the preparation of charcoal include, choerospondias axillaris (lapsi), seeds coconut plant, evergreen trees, deciduous trees, pine, and oak, to name a few (2 – 6). Charcoal, in general, is prepared by heating the animal and plant products at a relatively higher temperature, 600 ºC for carbonization to take place, preferably in an inert atmosphere. At this high temperature, the moisture and carbon enriched products like fats, proteins, and other remains are incinerated to form a gas, and remains of unburned carbon are left, which is technically termed as charcoal (7). Charcoal has the *tremendous adsorption* potential to absorb moisture in the pores created during high-temperature burning. Carbon-containing materials like hardwood trees, coconut shells, etc. heated within a certain restricted amount of air and converted to black substance, which is very porous and soft popularly known as activated charcoal. When such activated charcoals are grinded to powder form they contain very small carbon particles having a larger surface area, so that they have a high affinity for organic compounds like dyes, pesticides, germicides, etc. (6, 7). PZC is called as the pH for which the substance under consideration has net neutrality, i.e., to say neutral charge. One of the most significant qualities of PZC is that the substance under consideration has a positive charge below PZC pH and negative charge beyond PZC pH. This unique feature of having positive and negative charge allows anions and cations to be adsorbed on the surface of charcoal (8, 9). Every mineral or its crystalline structure possess a PZC, though the measurement of this PZC property is difficult and values as well as names for the property vary, and sometimes referred to as g point of zero charges and sometimes even as point of zero net proton charge (10-14). It was reported earlier that the pH value of PZC for activated carbon WHK as 2.5 (1). Below the PZC, i.e. at pH< 2.5; the surface becomes positive whereas the surface becomes negative for pH above 2.5 as weakly acidic oxygen-containing groups get dissociated.

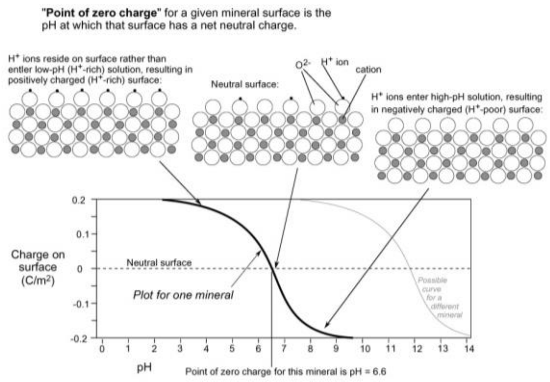

Figure 1. An explanation of PZC (15). Copyright permission from L. Bruce Railsback, Department of Geology, University of Georgia, Athens, Georgia 30602-2501 U.S.A.

Production and use of charcoal can be tremendous importance for industrial purposes, medicinal purposes and scientific researches in developing countries like Nepal. Yet, there are not so many works found on literature related to PZC of charcoals (8, 16 - 17) and there is no work of PZC of charcoals from the trees locally found in Nepal. So, the present work aims to determine the pH of the point of zero charge of two varieties of homemade charcoals made from trees locally found in Nepal, *Shorea robusta,* and *Pinus roxburghii* by pH drift method at room temperature (300 ± 2 K).

The pH drift is a quick and reliable method for the determination of PZC and is believed to be appropriate for charcoal. For this method, the solution of $CaCl_2$ was boiled to separate dissolved CO_2 and then cooled at room temperature. By using NaOH or HCl, the pH was modified to a value between 10 and 2. Charcoal was mixed into the pH-modified solution in a capped vial and kept 24 h for equilibrium. By measuring the final pH and it varied with the initial pH. There was the crossing of the final pH versus the initial pH. The crossing point for pH final line is considered as PZC (18).

II. MATERIALS AND METHODS

Activated charcoal (Merck, India) available in the laboratory of Central campus of Technology, Hattisar, Dharan and two samples of different woods of *Shorea robusta* and *Pinus roxburghii* of locally available trees in the forest nearby Dharan, Sunsari, Nepal were collected and their charcoals were prepared. Collected dry wood pieces were further allowed to dry in air for seven days. They were cut into small pieces of dimensions of about 10 inches, packed into a tin can and covered and were provided only with small holes to allow passage of limited air and smokes to escape. It was kept in another bigger drum made up of iron covered with other burning materials like papers, dry grasses, and dry woods and burnt for about three hours, followed by cooling. The pieces were then collected in clean plastic bags. To activate thus obtained carbon wooden charcoals were heated in absence of air. It was baked again in the presence of an oxidizing gas such as oxygen, carbon dioxide, and steam. Pieces of charcoals were grinded into powder form. Powder samples were kept in hermetically sealed weighing bottles and these bottles were kept inside desiccators to prevent moisture absorption.

The pH of PZC was studied by pH drift method using a glass electrode (pH 2700, Eutech instruments, Singapore) calibrated by buffers of pH 4, 7 and 10(16). For the determination of PZC, 20 ml of a 0.01M NaCl solution was kept in a capped 100ml conical flask (Pyrex glass). The pH was then modified to a consecutive integer from 2 to 10, by carefully adding the required amount of either 0.1M HCl or 0.1M NaOH using a micropipette (10-200µL and 100-1000µL capacity).

The powdered samples of charcoal 0.15g were added to the solution in a conical flask, capped and placed in the shaker. The final pH of all charcoal samples, measured after 24 hours were plotted against initial pH to calculate PZC. The pH in which the curve crosses the $pH_{initial} = pH_{final}$ line is considered as values of PZC of corresponding charcoal at room temperature 300.15 ± 2 K as the method used by others (19). The experiments were performed in triplicates. For the preparation of standard solutions of required chemicals, triple distilled water having a conductance less than 10^{-6} S cm^{-1} at 300.15 K was used.

III. RESULTS AND DISCUSSION

The pH of points of zero charge for the chosen homemade charcoals of *Shorea robusta* and *Pinus roxburghii* and activated charcoals are respectively 2.9, 4.1 and 5.0 as tabulated in Table 1. Since the PZC of these homemade charcoals are below 7, they have perfect charge balance in the acidic region. The acidic water donates more H^+ than OH^- groups and the surface of these homemade charcoals are positively charged and can attract anions.

Table 1. PZC values of homemade charcoals and activated charcoals at room temperature.

S. No.	*Adsorbents*	*[NaCl] mole L^{-1}*	*PZC*
1.	*Shorea robusta* (Local name: *Sakhuwa*)	0.01	2.9
2.	*Pinus roxburghii* (Local name: *Salla*)	0.01	4.1
3.	Activated Charcoal (Merck, India)	0.01	5.0

The graph was analyzed by the use of an easy plot program. Figure 2 shows the plots of initial pH values and final pH values. The dashed line passing through the middle of two axes intersects all these three curves at three different points respectively at 2.9, 4.1 and 5.0. These are the values where initial pH = final pH. Thus, these points indicate PZC values of homemade charcoals of *Shorea robusta* and *Pinus roxburghii* and commercial activated charcoal respectively. The curves of all the samples of charcoals are almost in an increasing manner with only a few points slightly increased and slightly decreased. These small variations may be due to small variations of room temperatures when performing experiments. Scientists have reported a variation of PZC values of some charcoals is due to variation of the ionization constant of water with temperature (8,17). It may be also because of not performing experiments in an inert atmosphere. The result is shown in figure 3 also predicts that the positive charge surfaces of charcoals follow the increasing order: Activated charcoal<*Pinus roxburghii*<*Shorea robusta*. Thus, anion adsorption on the surface of these charcoal increases in the order Activated charcoal<*Pinus roxburghii*<*Shorea robusta.*

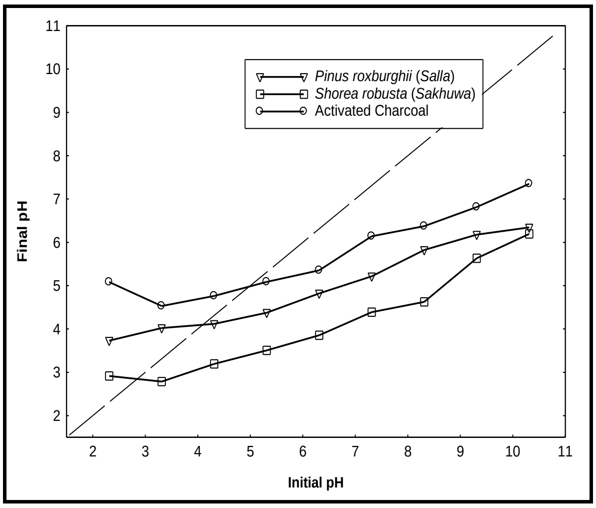

Figure 2. PZC of activated charcoal, and homemade charcoal of *Shorea robusta* (Local name: *Sakhuwa*) and *Pinus roxburghii* (Local name: *Salla*)

IV. CONCLUSIONS

Experimental measurements of pH of the different homemade charcoals of *Shorea robusta* and *Pinus roxburghii* shows that their PZC values are less than that of commercial activated charcoal. These experimental results predict that these homemade charcoals can be used as adsorbents in acidic regions. Such charcoals upon activation can be used in soils for pesticide inactivation, as a medicinal antidote for poisoning and drinking water filtration.

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