Optimization of Arsenic Removal from Aqueous Solution Using Indigenously Prepared Biosorbents from Fruit Peels through Response Surface Methodology

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Abstract
Sorption potential of the indigenously prepared biosorbents from orange, melon and banana peels were optimized for arsenic. The responses were generated using response surface methodology (RSM), results indicated a significant model with three sources of biosorbents was also influencing the levels of arsenic sorption significantly. The high R^2 value (above 90%) indicating a good reliability of model and explained greater than 90% of variability among collected data. Linear effect of biosorbent dose concentrations (mg) were observed on the sorption efficiency for As. However, the sorption efficiency reduces significantly after the interaction time of 120 minutes. Under optimized predicted model actual experiment revealed that melon peel biosorbent uptake the 96.5mg, orange peel biosorbent uptake 83.5mg, and banana peel biosorbent uptake the 80.25mg of As. The response surface methodology showed that the indigenously prepared biosorbents had a great potential for removal of arsenic from water. And the sorption potential was greater in melon peel as compared to orange peel and banana peel respectively.

Keywords: Fruit peels; Biosorbent, Heavy metals; Response surface Methodology

Introduction
Drinking water quality and purity must be regularly monitored in order to maintain a healthy community. Various water treatment programs, such as membrane filtration, reverse osmosis, ion exchange, electrodialysis and precipitation, may be used to remove contaminants from drinking water. These treatments were selected and implemented keeping in view the quality of physicochemical and microbiological parameters present in the water. The most current method for removing pollutants from drinking water is a contemporary approach that is based

on sorption. Biosorption is a new approach for scavenging contaminants such as metal ions and other elements from the aqueous solution by the help of moderately active, organic biomass due to the "high attractive forces" that exist between the biosorbent and sorbate (Kabir & Chowdhury, 2017). Several biosorbents have been used over the past few years to remove heavy metals from water and these were obtained from variety of sources such as fish scales, crab shells, lignin, fruit peels, plant parts, bark, microbial and algae biomass, including that of bacteria, fungi, and yeast were also employed for sorption of contaminants from aqueous solutions (Madela & Skuza, 2021). The main benefits of biosorption over other conventional treatment techniques are its high efficacy, cheap cost, low nutritional needs, biosorbent regeneration, decrease in chemical and biological sludge, and fine potential for metal removal (Ngo et al., 2015).

A tremendous quantity of agricultural food wastes and byproducts were generated worldwide every year, particularly throughout the production chain. Agricultural materials were better and abundantly available biosorbent sources as they contain proteins, hydrocarbon, starch, polysaccharides and lignin in their composition and these compounds have variety of functional groups that have the ability to sequester metals from water by forming chelates or by adsorption linkage. Agricultural waste materials being abundantly available, having unique composition, free in cost and ecofriendly seemed to be an actual and sustainable option for preparation of biosorbents. Using agricultural wastes has an additional advantage that unlike living biomass no growth media and nutrients are required for their maintenance which will deduct the overall operational cost (Burakov et al., 2018).

Biosorption mechanisms vary and are not completely understood due to the biological complexity of biosorbents (Syeda et al., 2022). Some of the key mechanisms that were involved in the sorptions includes physical adsorption by week van der wall forces, chemisorption through creation of strong chemical bounds, attachment of surface functional groups, ion exchange mechanism, formation of complexations, pore entrapment and microbial activity that produces polymeric substances that can bind and sequester contaminates. The biosorbtion process was influenced by multiple factors such as pH, temperature, contact time, biosorbent dosage, initial contaminant concentration, and environmental conditions (Ahmad & Azam, 2019).

The use of organic waste material directly as a biosorbents may have some problems like low adsorption capacity, and low efficiency so the biosorbents have to undergo through number of pre-treatment, activation and modification steps that can increase their adsorption capacity, porosity and surface area for maximum contaminant removal efficiency (Nguyen et al., 2013). The activation can be achieved by the washing the biosorbent with acid or alkali that can increase its capacity to adsorb cations and anions respectively (Chiban et al., 2012). In Pakistan agriculture waste material is generated in huge amounts and were not managed properly or some time sold out in lieu of very short amount of cash or burned out posing serious environmental issues so the techniques like sorption and preparation of sorbents can give an extra advantage to farmers and industrialist to earn a good amount of revenue from the sale of their organic waste produce as a biosorbent (Okafor et al., 2012). So The present research study was designed to evaluate and the potential of indigenously prepared biosorbents of (orange, banana and melon) peels for the removal of arsenic (As) and to optimize the biosorbent concentration and interaction time for the sorption using the response surface methodology.

Materials and Methods

Preparation of Biosorbents

After properly washing the fruit peels in distilled water, all dirt, dust, or foreign pollutants were eliminated. The selected fruits peels of orange, melon and banana were dehydrated at 65^{o} C, the dried peels were soaked in phosphoric acid for activation and then charred in muffle furnace 600^{o} C before ground to fine powder biosorbent (Joseph et al., 2019).

Analytical Examination

For this experiment, analytic grade chemicals were used. Arsenic metal salt was dissolved in the appropriate volumes of distilled water to create stock solutions of 1000 mg L^{-1}. Further dilutions and sub stock solutions were prepared by using distilled water. The determination of arsenic level in various treatments were carried out by using already reported inductive coupled plasma (ICP) method (Ammann, 2002).

Optimization Of Adsorption Capacity Of Biosorbent Using Response Surface Methodology

Optimization of adsorption capacity of biosorbents were carried out using the standard protocols (Jaafari & Yaghmaeian, 2019). The coded and uncoded level of independent variables used were shown below in Table 1.

Categories of Biosorbents

1. Orange peel

2. Banana peel
3. Melon peel

Table 1. Coded and un-coded level of independent variables used in adsorption capacity optimization for heavy metals.

Independent Variable	-1	0	+1
Biosorbent Dose (mg)	50	100	150
Contact Time (Minutes)	60	120	180

Results and Discussion

The design expert 7 was used to prepare a quadratic model of central composite design for two variable factors biosorbent concentration (mg) and Interaction time (minutes) and third categorical factor type of sorbent that include, melon peel biosorbent, banana peel biosorbent and orange peel biosorbent. Using the planed designed of Response Surface Methodology (RSM), 39 different runs were planned to analyze the sorption response of biosorbents for arsenic (As).

Arsenic Sorption by Indigenously Prepared Biosorbents

The mean squares for the model parameters in Table 2 were displayed in the variance analysis for arsenic sorption. The model is significant, according to the model's F-value of 1246.01. Model terms A (biosorbent concentration), B (interaction time), and C (sorbent type) were significant, were indicated by values of "Prob > F" less than 0.0500. The "Lack of Fit F-value" of 0.83 indicates that, in comparison to the pure error, the Lack of Fit is not significant which made model suitable to use. There was a fair amount of agreement between the "Adjusted R-Squared" of 0.9972 and the "Predicted R-Squared" of 0.9954

Source	Sum of Squares	df	Mean Square	F Value	p-value
Model	26497.32	11	2408.847	1246.011	< 0.0001
A-Biosorbent Conc.	23714.79	1	23714.79	12266.82	< 0.0001
B-Interaction Time	1667.243	1	1667.243	862.4056	< 0.0001
C-Type of sorbent	513.5244	2	256.7622	132.814	< 0.0001
Residual	52.19765	27	1.933246		

Lack of Fit	26.50873	15	1.767249	0.82553	0.6425
Pure Error	25.68892	12	2.140743		

Table 2. Variance analysis for response surface quadratic model for arsenic sorption

p-value < 0.05 = Significant and p-value > 0.05 = Non Significant

Arsenic Sorption by the Indigenously Prepared Orange Peel Biosorbent

The 3D - surface graph for the sorption of arsenic by the indigenously prepared orange biosorbents was showed in Figure 1. The minimum sorption of As was 22mg at the biosorbent concentration of 50mg and interaction time of 60minutes the sorption concentration of As increases significantly to 35.75mg and 42mg as the interaction time was increased to 120 minutes and 180 minutes respectively at the constant biosorbent concentration of 50mg. At the biosorbent concentration of 100mg and 150mg the arsenic sorption was increased to 51.5mg and 85mg respectively keeping the interaction time constant at 60 minutes. The maximum sorption of arsenic 117.43mg was found at the biosorbent concentration of 150mg and interaction time of 180 minutes. The result showed the linear effect of biosorbent concentration and interaction time on the sorption of arsenic by orange peel biosorbent. Similar findings were also detected by Gutha et al., (2011) who used various plant parts as a biosorbent for the removal of heavy metals, in their study they have identified that the sorption capacity of the biosorbent is directly related to the biosorbent dose. The regression equation for the arsenic sorption by orange peel biosorbent was prepared as equation 1.

$$Arsenic\ (As)\ Sorption\ for\ Orange\ peel\ biosorbent\ =\ [-26.22228\ +\ 0.42860\ (A) +\ 0.41938\ (B) +\ 6.32250 - 004(AB) +\ 9.48377 - 004\ (A2) - 1.07664 - 003\ (B2)] \ldots\ldots\ldots \text{Equation 1}$$

Where (A) represents the biosorbent concentration and (B) represents the interaction time by using the equation 1, we can estimate the arsenic sorption capacity for orange peel biosorbent at any level of concentration and interaction time.

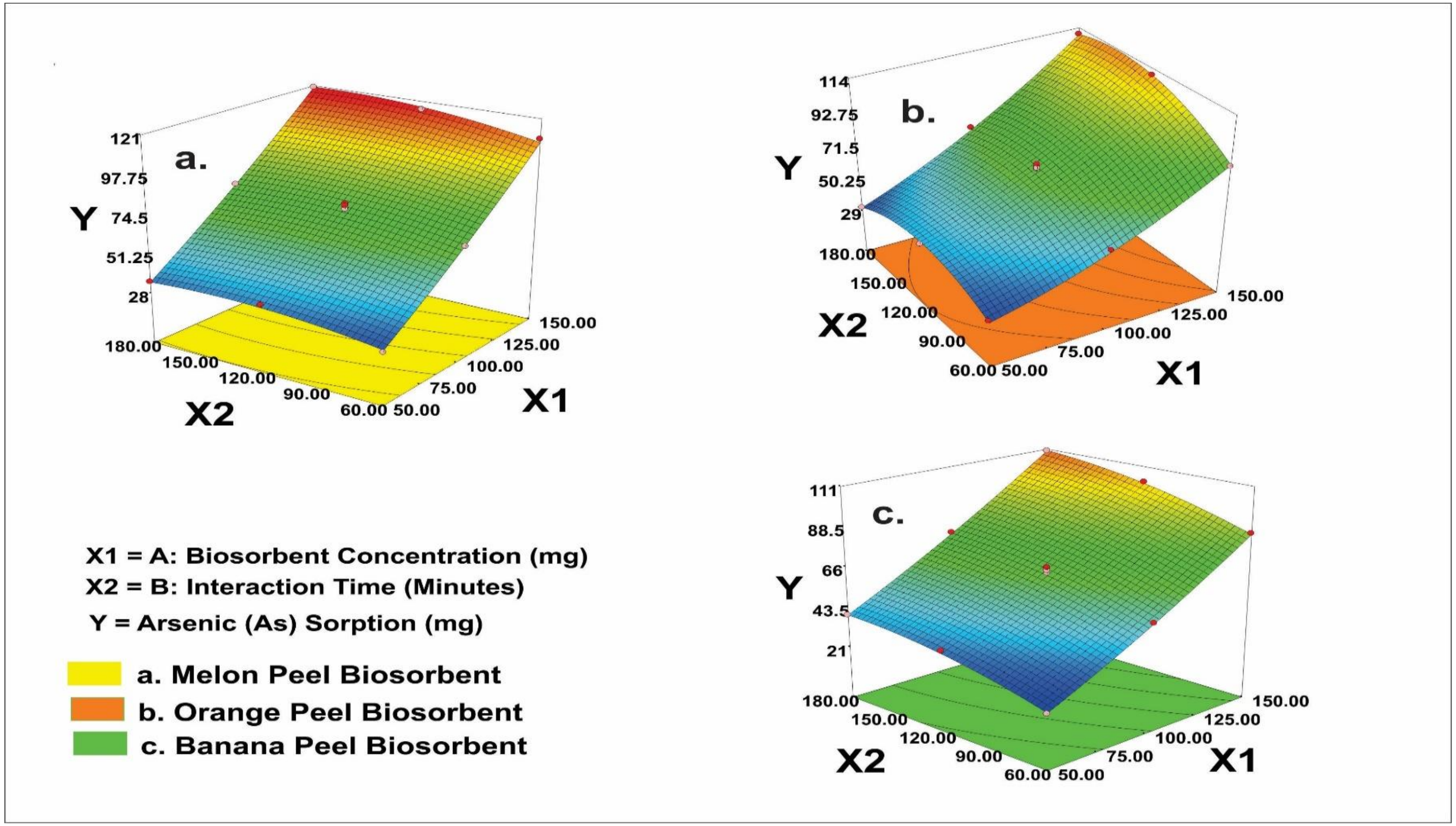

Figure 1: 3D-Surface graphs for sorption of arsenic by **a.)** melon peel biosorbent, **b).** orange peel biosorbent and **c.)** banana peel biosorbent

Arsenic Sorption by the Indigenously Prepared Melon Peel Biosorbents

The 3D - surface graph for the sorption of Arsenic by the indigenously prepared melon biosorbents is shown in Figure1. The minimum sorption of As is 28mg at the biosorbent concentration of 50mg and interaction time of 60 minutes the sorption concentration of As increases significantly to 37.5mg as the interaction time increased to 120 minutes at constant biosorbent concentration of 50mg. The sorption capacity of melon peel biosorbent slightly reduced to 35mg as the further interaction time is increased from 120 minutes to 180 minutes at the constant biosorbent concentration of 50mg. At the biosorbent concentration of 100mg and 150mg the arsenic sorption increased to 65mg and 109mg, respectively keeping the interaction time constant at 60 minutes. The maximum sorption of Arsenic 120mg was found at the biosorbent concentration of 150mg and interaction time of 180 minutes. The results showed the linear effect of melon peel biosorbent concentration on the sorption capacity sorption increases with increase in biosorbent concentration and a slight reducing effect on the sorption with the increase in interaction time was observed especially after 120 minutes. The reduction in the sorption over a long period of interaction time between the sorbate and biosorbent was also recorded by Park et al. (2008) and the reason for this phenomena was due to the presence of week vander wall forces that were involved in the binding of sorbate to biosorbent was not able to hold the sorbate for longer time, agitation speed in the process can also effect the sorption capacity. The regression equation for the estimation of arsenic sorption by melon peel biosorbent was identified as equation 2 where (A) represented the biosorbent concentration in milligrams and (B) showed interaction time in minutes.

$$\begin{aligned} Arsenic\ sorption\ by\ melon\ peel\ biosorbeent \\ = [-14.87923 + 0.54945\,(A) + 0.27295\,(B) + 6.32250 \\ - 004(AB) + 9.48377 - 004\,(A2) - 1.07664 \\ - 003\,(B2)] \ldots\ldots\ldots\ldots\ldots\ldots.\text{Equation 2} \end{aligned}$$

Arsenic Sorption by the Indigenously Prepared Banana Peel Biosorbents

The 3D surface graph for the sorption of Arsenic by the indigenously prepared banana biosorbents was showed in Figure 1. The minimum sorption of As was 21.3mg at the biosorbent concentration of 50mg and interaction time of 60 minutes the sorption concentration of As increases significantly to 36.17 mg and 39.5mg as the interaction time was increased to 120 minutes and 180 minutes respectively. At the biosorbent concentration of 100mg and 150

mg the arsenic sorption was found to be as 51.3mg and 85.38mg respectively keeping the interaction time constant at 60 minutes. The maximum sorption of Arsenic 110mg was found at the biosorbent concentration of 150mg and interaction time of 180 minutes. The results showed that with the increase in biosorbent concentration the increase in sorption was observed. However, at the lower interaction times sorption was more which reduced significantly with the increase in interaction time. The results of our findings were in line with findings of Owamah, (2014) who uses banana peel for the sorption of heavy metals from the aqueous solution. The regression equation for the arsenic sorption by banana peel biosorbent was presented as equation 3, where (A) was represented for biosorbent concentration in milligrams and (B) showed interaction time in minutes.

$$\begin{aligned} &\textit{Arsenic sorption by banana peel biosorbent} \\ &\quad = [-21.13959 + 0.40314\,(A) + 0.3743\,(B) + 6.32250 \\ &\quad - 004(AB) + 9.48377 - 004\,(A2) - 1.07664 \\ &\quad - 003\,(B2)] \ldots\ldots\ldots\ldots\ldots\ldots \text{Equation 3} \end{aligned}$$

Optimization of Arsenic Sorption by Indigenously Prepared Biosorbents Using Response Surface Methodology

The optimization procedure for indigenously prepared biosorbents was carried out using the response surface methodology (RSM) by design expert 7. The optimization goals were set in the optimization numerical for three categorical factors that is the type of biosorbent. First planned goal was to minimize the use of biosorbent concentration and interaction time. The second goal that was planned is to maximize the sorption of response variables arsenic. The optimization numerical is shown in table 3.

Table 3. Optimization numerical

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight
Biosorbent Concentration	Minimize	50	150	1	1
Interaction	Minimize	60	180	1	1

Time					
Arsenic	Maximize	21.3	120	1	1

The optimization numerical was analyzed and one optimized solution was suggested by the software for each categorical factor, the predicted selected solution was showed in table 4.

Table 4. Predicted selected solutions versus actual experimental values for arsenic sorption by indigenously prepared biosorbents

Type of biosorbent	Biosorbent Concen. (mg)	Interaction Time (min)	As Sorption (mg)	
			Predicted	Actual
Melon Peel	128.06	95.99	95.08	96.5
Orange Peel	127.72	110.37	86.07	83.5
Banana Peel	128.18	111.05	83.41	80.25

The actual experiment for sorption of Arsenic was performed using the suggested optimized biosorbent concentration and interaction time as showed in Table 4. The actual results of optimization were found to be close to the predicted results. Under optimized conditions melon peel biosorbent at the biosorbent concentration of 128.06mg and at the interaction time of 95.99 minutes uptake the 96.5mg of As. The orange peel biosorbent at the biosorbent concentration of 127.72mg and interaction time of 110.37 minutes should successful potential to uptake 83.5mg of As. The Banana Peel biosorbent at the concentration of 128.18mg and interaction time of 111.05 minutes successfully uptake the 80.25mg of Ni, Pb and As. The results showed that the sorption potential of indigenously prepared melon peel biosorbent was higher than the orange peel biosorbent which was followed by the banana peel biosorbent that showed less sorption potential in comparison.

Conclusion

Three biosorbents were prepared indigenously using melon peel, orange peel and banana peel and their sorption potential was investigated and optimized for arsenic (As) using the response surface methodology (RSM), central composite design, quadratic model, the results indicated a significant model with three sources of biosorbents were also influencing the levels of As sorption significantly. A high R^2 value (above 90%) indicating a good reliability of model and explaining more than 90% of variability of collected data, overall a linear effect of independent variables i.e.; (biosorbent dose concentration (mg) and interaction time (minutes)) was visible for As sorption. The RSM showed that the indigenously prepared biosorbents have a great potential for removal of As from water. Under optimized conditions melon biosorbent at the biosorbent concentration of 128.06 mg and at the interaction time of 95.99 minutes, uptake the 96.5mg of As. The orange peel biosorbent at the biosorbent concentration of 127.72mg and interaction time of 110.37 minutes had potential to uptake 83.5mg of As. The banana peel biosorbent at the concentration of 128.18mg and interaction time of 111.05 minutes, uptake the 80.25mg of As. The results showed that the sorption potential of indigenously prepared biosorbents of melon peel > orange peel > banana peel. The regression equations 1, 2 and 3 generated during the present study may be used in the future research studies in order to identify and compare the sorption potential for respective biosorbents.

Refer5ences

Ahmad, A., & Azam, T. (2019). Water purification technologies. In A. M. Grumezescu & A. M. Holban (Eds.), *In bottled and packaged water* (pp. 83-120). Cambridge, UK: Woodhead Publishing

Ammann, A. A. (2002). Speciation of heavy metals in environmental water by ion chromatography coupled to ICP–MS. *Analytical and Bioanalytical Chemistry*, *372*(3), 448-452.

Burakov, A., Galunin, E., Burakova, I., Kucherova, A., Agarwal, S., Tkachev, A., & Gupta, V. (2018). Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review. *Ecotoxicology and Environmental Safety*, *148*, 702-712.

Chiban, M., Zerbet, M., Carja, G., & Sinan, F. (2012). Application of low-cost adsorbents for arsenic removal. *Journal of Environmental Chemical Ecotoxicology*, *4*, 91-102.

Gutha, Y., Munagapati, V. S., Alla, S. R., &Abburi, K. (2011). Biosorptive removal of Ni (II) from aqueous solution by *Caesalpinia bonducella* seed powder. *Separation Science and Technology*, *46* (14), 162-166

Jaafari, J., & Yaghmaeian, K. (2019). Optimization of heavy metal biosorption onto freshwater algae (*Chlorella* coloniales) using response surface methodology (RSM). *Chemosphere*, *217*, 447–455

Joseph, L., Jun, B. M., Flora, J. R., Park, C. M., & Yoon, Y. (2019). Removal of heavy metals from water sources in the developing world using low-cost materials: A review. *Chemosphere*, *229*, 142–159

Kabir, F., & Chowdhury, S. (2017). Arsenic removal methods for drinking water in the developing countries: technological developments and research needs. *Environmental Science and Pollution Research International*, *24*(31), 24102–24120.

Madela, M., & Skuza, M. (2021). Towards a circular economy: Analysis of the use of biowaste as biosorbent for the removal of heavy metals. *Energies*, *14*(17), 24-27.

Ngo, H. H., Guo, W., Zhang, J., Liang, S., Ton-that, C., & Zhang, X. (2015). Typical low cost biosorbents for adsorptive removal of specific organic pollutants from water. *Bioresource Technology*, *182*, 353-363

Nguyen, T. A. H., Ngo, H. H., Guo, W. S., Zhang, J., Liang, S., Yue, Q. Y., & Nguyen, T. V. (2013). Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. *Bioresource Technology*, *148*, 574-585.

Okafor, P. C., Okon, P. U., Daniel, E. F., & Ebenso, E. E. (2012). Adsorption capacity of coconut (*Cocos nucifera* L.), shell for lead, copper, cadmium and arsenic from aqueous solutions. *International Journal of Electrochemical Science*, *7*, 12354-12369.

Owamah, H. I., Dahunsi, S. O., Oranusi, U. S., & Alfa, M. I. (2014). Fertilizer and sanitary quality of digestate biofertilizer from the co-digestion of food waste and human excreta. *Waste Management*, *34*(4), 747-752.

Park, D., Lim, S. R., Yun, Y. S., & Park, J. M. (2008). Development of a new Cr (VI)-biosorbent from agricultural biowaste. *Bioresource Technology*, *99*(18), 8810–8818

Syeda, H. I., Sultan, I., Razavi, K. S., & Yap, P. S. (2022). Biosorption of heavy metals from aqueous solution by various chemically modified agricultural wastes: A review. *Journal of Water Process Engineering*, *46*, 102446

SUPPLIMENTARY TABLE AND MATERIAL

			Factor 1	Factor 2	Factor 3	Response
Std	Run	Block	A:Biosorbent Concentration	B:Interaction Time	C:Type of Peel Biosorbent	Arsenic Sorption
			(mg)	minutes		(mg)
8	1	Block 1	100	180	Orange	79.874
16	2	Block 1	50	180	Melon	35
38	3	Block 1	100	120	Banana	66.52
19	4	Block 1	150	120	Melon	116
27	5	Block 1	50	60	Banana	21.3
28	6	Block 1	150	60	Banana	85.382
31	7	Block 1	50	120	Banana	36.165
11	8	Block 1	100	120	Orange	70
4	9	Block 1	150	180	Orange	117.343
34	10	Block 1	100	180	Banana	73
17	11	Block 1	150	180	Melon	120
22	12	Block 1	100	120	Melon	76
14	13	Block 1	50	60	Melon	28
6	14	Block 1	150	120	Orange	105.6
29	15	Block 1	50	180	Banana	39.5
30	16	Block 1	150	180	Banana	110
32	17	Block 1	150	120	Banana	102.19
7	18	Block 1	100	60	Orange	51.5
33	19	Block 1	100	60	Banana	51.3
36	20	Block 1	100	120	Banana	65.5
5	21	Block 1	50	120	Orange	35.7
35	22	Block 1	100	120	Banana	62.5
24	23	Block 1	100	120	Melon	72.75
37	24	Block 1	100	120	Banana	64.8
25	25	Block 1	100	120	Melon	76
2	26	Block 1	150	60	Orange	85
26	27	Block 1	100	120	Melon	74.75
13	28	Block 1	100	120	Orange	69.5
9	29	Block 1	100	120	Orange	68
3	30	Block 1	50	180	Orange	42
21	31	Block 1	100	180	Melon	75
10	32	Block 1	100	120	Orange	67.75
39	33	Block 1	100	120	Banana	66.5
1	34	Block 1	50	60	Orange	22
12	35	Block 1	100	120	Orange	67.6
18	36	Block 1	50	120	Melon	37.5
15	37	Block 1	150	60	Melon	109
23	38	Block 1	100	120	Melon	73
20	39	Block 1	100	60	Melon	65